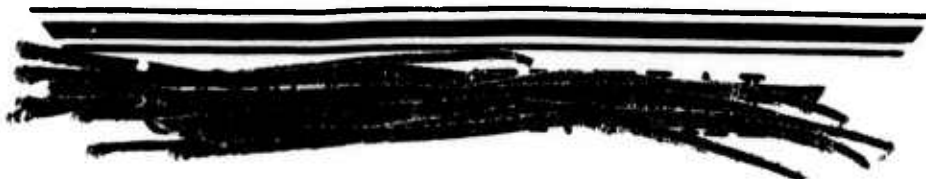| AD NUMBER	
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June 1962
Report No. 0235-01-14
(Quarterly)
Copy No. *AF-12-V*

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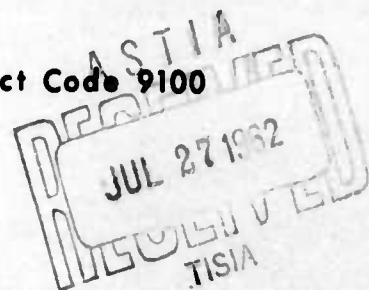# RESEARCH IN FLUORO-NITRO COMPOUNDS

Contract Nonr-2655(00)
ARPA Order No. 170-61, Project Code 9100

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Chemical Products Division

JUL 27 1962

Aerojet-General ® CORPORATION

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June 1962

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(Quarterly)

RESEARCH IN FLUORO-NITRO COMPOUNDS

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Chemical Products Division

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ABSTRACT

A prolonged reaction of acetonylacetone with difluoramine in sulfuric acid gave 2,2,5,5-tetrakis(difluoramino)hexane, 2,5-dimethyl-2,5-bis(difluoramino) tetrahydrofuran, and, apparently, a new isomer of the latter. Ethyl 5-keto-hexanoate gave ethyl 5,5-bis(difluoramino)hexanoate.

The cyclohexene adduct of difluoramine was prepared using either sulfuric acid or methanesulfonic acid as the catalyst.

The reaction of $\underline{t}$-pentanol with difluoramine in sulfuric acid gave a mixture of acetone and methyl ethyl ketone.

The reaction of ethyl N-fluorocarbamate with $\underline{n}$-butylnitramine in sulfuric acid gave N-$\underline{sec}$-butyl-N-fluorocarbamate.

The NMR spectrum of the product of the reaction of ethyl N-fluorocarbamate with hot concentrated sulfuric acid agreed with that expected for N-fluoroammonium ion. That of the analogous product from ethyl N-fluoro-N-methylcarbamate was as expected for N-fluoro-N-methylammonium ion. These products reacted with aqueous cyclohexanone to give caprolactam and N-methylcaprolactam.

The adducts of ethyl N-fluorocarbamate with cyclohexene and cyclopentene were prepared.

The nitration of methyl N-$\underline{n}$-butylcarbamate gave N-fluoro-N-$\underline{n}$-butylamine.

The reaction of ethyl N-fluorocarbamate with sodium methoxide gave the ethyl methyl ester of iminodicarboxylic acid.

Fluorination of aqueous ε-caprolactam gave 6-difluoraminohexanoic acid. This acid could be dissolved without decomposition in aqueous sodium bicarbonate, but was dehydrofluorinated by cold aqueous alkali. Ethyl 6-difluoraminohexanoate was prepared by esterification of the acid.

Direct fluorination of the cyclohexene N-fluorocarbamate adduct gave difluoraminocyclohexane.

CONTENTS

CONTENTS (cont.)

I.   INTRODUCTION

The objective of this program is to develop new methods of preparing high-energy materials of interest for military applications. During this report period work was continued on the alkylation reactions of difluoramine, the aqueous fluorination reaction, and reactions of fluorocarbamates.

II.   TECHNICAL DISCUSSION

A.   REACTIONS OF DIFLUORAMINE (K. Baum)

1.   Discussion

a.   Carbonyl Compounds

During the past year a rapid screening has been made of the addition reactions of difluoramine in sulfuric acid to carbonyl compounds, including a variety of configurations and functional substituents. Although the preparation of gem-difluoramines appeared to be general for simple ketones and aldehydes, many substituents prevented this reaction by either reducing the reactivity of the carbonyl or participating in cyclization reactions. In the preceding report period a more thorough study of some of these reactions was begun. Thus, under appropriate experimental conditions, polynitroketones, which were previously found to be unreactive, could be converted to gem-difluoramines.*

The reaction of acetonylacetone has now also been re-examined. This reaction previously yielded 2,5-dimethyl-2,5-bis(difluoramino)-tetrahydrofuran when it was carried out with refluxing difluoramine over concentrated sulfuric acid at atmospheric pressure.**

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* Aerojet-General Report No. 0235-01-13, March 1962, p. 1 (Confidential).
** Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 6 (Confidential).

II Technical Discussion, A (cont.)   Report No. 0235-01-14

$$CH_3COCH_2CH_2COCH_3 \longrightarrow CH_3 - \underset{NF_2}{\overset{CH_2 - CH_2}{\underset{|}{C}}} \underset{O}{\overset{}{}} \underset{NF_2}{\overset{|}{C}} - CH_3$$
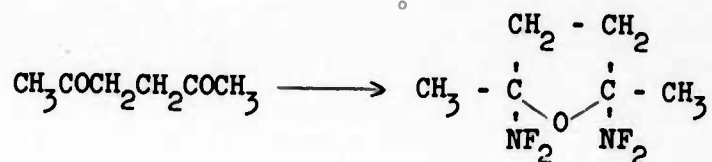
One would expect that this ring should be opened in a more acidic medium, at a higher temperature, or with a prolonged reaction time. The use of a pressure reactor to achieve a longer reaction time and a higher temperature than are practical with refluxing difluoramine was therefore investigated.

This method involved experimental difficulties in that acetonylacetone is unstable in sulfuric acid, charring immediately, and therefore cannot be predissolved in the acid before the difluoramine is generated. Acetonyl-acetone was therefore added to a mixture of difluoramine and sulfuric acid in a pressure reactor cooled to -80°C. However, when the sealed reactor was allowed to warm to room temperature it was broken because of the heat released by the reaction. In order to avoid this problem, a two-stage reactor was used, in which the initial exothermic reaction was carried out at atmospheric pressure using difluoramine refluxing over concentrated sulfuric acid as a heat-transfer medium. The mixture was then drained into the pressure reactor containing fuming sulfuric acid. After a 40-hr reaction period, work-up gave a product which, although it distilled within a narrow temperature range, was found by gas chromatography to consist of four components.

The first component, in the order of retention times, was 2,5-bis(difluoramino)-2,5-dimethyltetrahydrofuran, identified by its infrared spectrum, which was identical to that of the product of the atmospheric pressure reaction.* The infrared spectrum of the second component (Figure 1) was very similar, differing slightly in the NF and ether regions. Nitrogen analysis indicates that it is an isomer of the above compound. Complete elemental and NMR analyses are not yet available. The third component, which comprised 60%

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* Aerojet-General Report 0235-01-10, 14 April 1961, Figure 7 (Confidential).

of the mixture, was identified as 2,2,5,5-tetrakis(difluoramino)hexane by its elemental analysis and infrared (Figure 2) and F^{19} (Figure 3) NMR spectra. The NMR spectra were obtained on a sample containing some acetonylacetone, the final component of the mixture.

In order to confirm the absence of a second isomer of the heterocyclic product in the atmospheric pressure reaction, this work was repeated. The reaction was quenched as soon as the addition of the ketone was completed. Gas chromatography of the product gave only the first peak.

The identification of the first two components of the pressure reaction mixture as cis-trans isomers would indicate that the initial reaction is stereospecific. Because of the interesting mechanistic consequences of this result, stress will be placed on the complete identification of these compounds.

The conversion of 2,5-bis(difluoramino)-2,5-dimethyltetra-hydrofuran to 2,2,5,5-tetrakis(difluoramino)-hexane may be represented as follows:
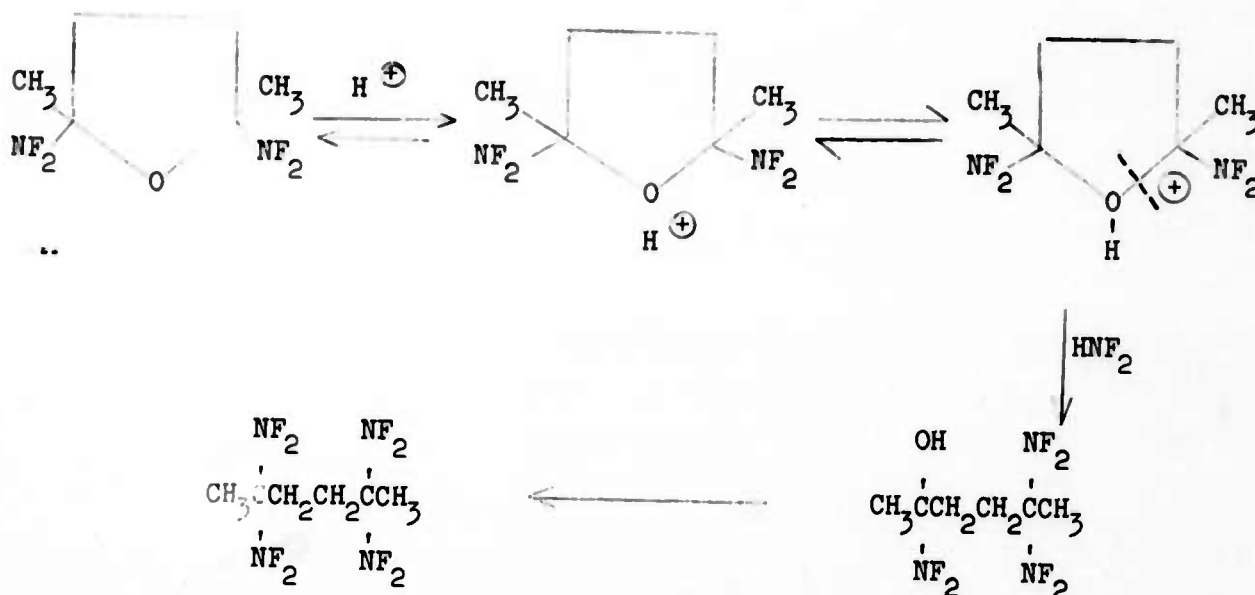
The reaction of ethyl 5-ketohexanoate with difluoramine was also carried out under conditions similar to those used for acetonylacetone;

the substrate was first added to refluxing difluoramine over sulfuric acid, and was
then sealed in a pressure tube containing fuming sulfuric acid. Work-up after 50
hr yielded ethyl 5,5-bis(difluoramino)-hexanoate of 96% purity, as analyzed by
capillary gas chromatography. The contaminant was starting material. Since the
boiling point was too high for preparative gas chromatography, this sample was
characterized directly by elemental analysis and by its infrared spectrum (Figure
5). This product is the first gem-difluoraminocarboxylic acid derivative, and will
be useful in determining the inductive effect of the gem-difluoramino grouping.

$$CH_3COCH_2CH_2CH_2CO_2Et \longrightarrow CH_3\overset{NF_2}{\underset{NF_2}{\overset{|}{\underset{|}{C}}}}CH_2CH_2CH_2CO_2Et$$
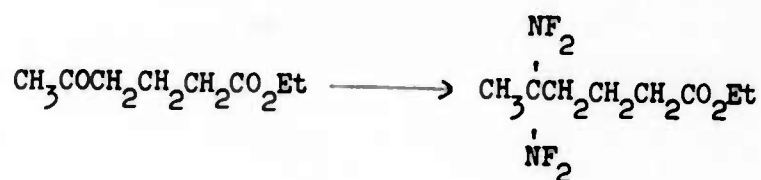
An attempt to extend this reaction to methyl levulinate
was unsuccessful. When a solution of this ester in sulfuric acid was treated with
difluoramine under pressure for 36 hr, only starting material and 4-difluoramino-γ-
valerolactone were recovered. The latter compound was prepared previously by the
reaction of levulinic acid with difluoramine.*

$$CH_3COCH_2CH_2CO_2CH_3 \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNF}_2} CH_3 - \overset{CH_2 - CH_2}{\underset{NF_2}{\overset{|}{\underset{|}{C}}}} \quad \overset{|}{\underset{O}{C}} = O$$
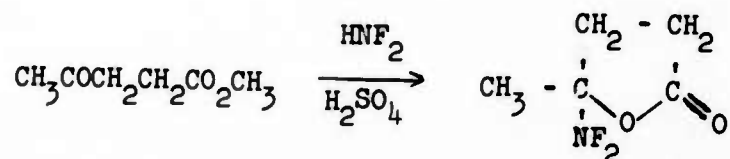
b.   Olefins and Alcohol

In the preceding report, the addition of difluoramine to
1-octene was described. This reaction has been extended to cyclohexene, to prepare

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*Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 12 (Confidential).

cyclohexyldiflu ramine.   The reaction was carried out in sulfuric acid. It was necessary to quench the reaction as soon as the addition of the olefin to the acid and difluoramine was finished in order to prevent decomposition of the adduct. Even so, the yield of cyclohexyldifluoramine was only 16%. This compound was identified by elemental analysis and by its infrared spectrum (Figure 6).

This addition also took place when methanesulfornic acid was used instead of sulfuric acid. In this case, cyclohexyl methanesulfonate was isolated as the major by-product. In order to determine whether this ester was an intermediate in the formation of cyclohexyldifluoramine, it was treated with excess difluoramine in the presence of a small amount of methanesulfonic acid. However, 90% of the ester was recovered unchanged, and no cyclohexyl-difluoramine was isolated.

Two attempts to add difluoramine to cyclopentene in sulfuric acid were unsuccessful. In both cases, the product fumed off when the last trace of extraction solvent was removed in the work-up.

Work was also continued on the reaction of t-alkyl carbonium ions with difluoramine in sulfuric acid. It was found previously* that t-butyldifluoramine reacts with sulfuric acid to give a nonvolatile intermediate which, on hydrolysis, yields acetone. The probable intermediate, 2-(difluoramino)-2-methyl-1-propanesulfonic acid, might be formed by the sulfonation of either t-butyldifluoramine or isobutylene with the subsequent addition of difluoramine.

This reaction has been extended to a higher homologue: t-Pentanol was reacted with difluoramine in sulfuric acid, and the reaction was continued until the initially formed t-pentyldifluoramine** layer disappeared. Quenching the reaction gave a mixture of methyl ethyl ketone and acetone, and

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* Aerojet-General Report No. 0235-01-13, March 1962, p. 4 (Confidential).

** Rohm & Haas Co., Report P-60-18, 18 November 1960, p. 22 (Confidential).

their monoadducts of difluoramine. Gas chromatography, which reversed this addition, showed that the ratio of acetone to methyl ethyl ketone was 3:1. This ratio is approximately that observed for 2-methyl-2-butene to 2-methyl-1-butene from El eliminations of t-pentyl derivatives.*

The characterization of the difluoramine adduct of crotonic acid was completed by obtaining the proton (Figure 7) and F^{19} (Figure 8) NMR spectra, which prove that the substituent is in the expected β position.

c.   Miscellaneous

The use of primary nitramines as alkylating agents in acidic media has been reported. Thus, dilute sulfuric acid** and nitric acid,*** respectively, gave the alcohol and nitrate, with the evolution of nitrous oxide.

This reaction was studied briefly as a method of preparing alkyldifluoramines. The reaction of n-butylnitramine with difluoramine, however, did not yield an isolatable product. The adduct was apparently rapidly decomposed in the sulfuric acid.

The use of ethyl N-fluorocarbamate as a model for difluoramine in this reaction was examined because similar reactions of the two reagents have been noted.**** The products of the former may be more stable.

The reaction of ethyl N-fluorocarbamate with n-butyl-nitramine gave ethyl N-sec-butyl-N-fluorocarbamate. The structure proof was based on analysis, and the infrared (Figure 9) and H^1 and F^{19} NMR spectra (Figures 10 and 11). The reaction thus proceeds through olefin formation or hydride shift to give the sec-butyl carbonium ion.

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*
C. K. Ingold, "Structure and Mechanism in Organic Chemistry," p. 442, Cornell University Press, Ithaca, N.Y., (1953).

**
H. van Erp, Rec. Trav. Chim., 14, 40 (1895).

***
A. P. N. Franchimont, ibid., 29, 296 (1910).

****
Aerojet-General Report 0235-01-13, March 1962, p. 12 (Confidential).

II Technical Discussion, A (cont.)

$$CH_3CH_2CH_2CH_2NHNO_2 \; + \; HNFCO_2Et \longrightarrow CH_3CH_2CH(CH_3)NFCO_2Et \; + \; N_2O$$
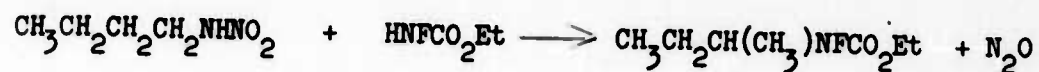
The reaction of t-butylhydroperoxide with difluoramine in sulfuric acid gave qualitative evidence for the formation of an O-NF$_2$ compound.* Two additional attempts to repeat this reaction resulted in explosions during the addition of the peroxide to difluoramine and sulfuric acid. This work has been discontinued.

2. Experimental

a. 2,2,5,5-Tetrakis(difluoramino)hexane

The apparatus for this reaction consisted of the standard glassware used for difluoramine reactions at reflux temperature at atmospheric pressure,** modified so that the contents of the reaction flask could be drained into a 100-ml heavy-walled glass tube with Fischer-Porter glass needle valves. The tube was immersed in a circulating bath. The tube contained a magnetic stirrer. The reaction was carried out remotely behind a steel barricade.

Acetonylacetone (2.32 g, 0.02 mole) was added dropwise to a refluxing mixture of 15 ml of concentrated sulfuric acid and approximately 7 g of difluoramine. When the addition was completed, and no further exothermic reaction was evident, the mixture was drained into the pressure reactor which had previously been loaded with 35 ml of 20% fuming sulfuric acid. The pressure reactor was cooled to -70°C to condense the difluoramine and the needle valves were then closed. The bath was allowed to warm to room temperature overnight, and on the following day the mixture was stirred for 7 hr.

After a total reaction period of 40 hr, the mixture was poured over 600 ml of ice, and the product was extracted with five 50-ml portions of methylene chloride. The methylene chloride solution was washed with 150 ml of water and dried over sodium sulfate. The solvent was distilled off, and vacuum distillation of the residue yielded 2.03 g of slightly yellow liquid, bp 70°/4mm. A viscous residue (1.4 g) remained in the pot.

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*Aerojet-General Report No. 0235-01-13, March 1962, p. 5 (Confidential).

** Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 10 (Confidential).

The distillate was found by gas chromatography (2.5-m column of 5% diethyleneglycol on Teflon, 85°C, 60 cc He/min) to consist of four components with the following retention times and relative areas: Compound A, 7 min, 13%; Compound B, 11 min, 13.1%; Compound C, 21 min, 59.9%; Compound D, 39 min, 13.9%. Analytical samples were prepared using this column. Earlier chromatographic work using a 2-m column of Teflon coated with 5% of a mixture of Apiezon L and diethyleneglycol adipate failed to separate compounds C and D, and this mixture was used for the NMR spectrum. Compound D was shown by its infrared and NMR spectra to be acetonylacetone. The infrared spectrum of Compound A was virtually identical with that of 2,5-bis(difluoramino)-2,5-dimethyltetrahydrofuran, previously prepared from acetonylacetone and refluxing difluoramine over sulfuric acid at atmospheric pressure.*

The infrared spectrum of Compound B (Figure 1) was similar to that of Compound A. The major difference was reduced absorption at 8.7 μ, although there were minor differences in the NF region. The nitrogen analysis of Compound A indicated an isomer of 2,5-bis(difluoramino)-2,5-dimethyltetrahydrofuran.

<u>Anal</u>. calcd. for $C_6H_{10}N_2F_4O$: N, 13.9. Found: N, 14.3.

The elemental analysis of compound C was in agreement with the structure 2,2,5,5-tetrakis(difluoramino)hexane.
<u>Anal</u>. calcd. for $C_6H_{10}N_4F_8$: C, 24.8; H, 3.45; N, 19.3. Found: C, 25.3; H, 3.75; N, 19.5.

The NMR spectra of compound C, contaminated by acetonylacetone, (Figures 3 and 4) confirmed this structure. The 56.4-mc F^{19} spectrum, obtained in carbon tetrachloride solution using fluorotrichloromethane as an internal reference, consisted of a signlet at -1500 cps. The 60-mc proton spectrum of a carbon tetrachloride solution with tetramethylsilane (TMS) as an internal standard shows a regular quintet at 8.37 (tau value) splitting approximately 2 cps, and a poorly resolved quintet at 7.72. Signals at 7.43 and 7.90 were shown to correspond to acetonylacetone. The infrared spectrum of 2,2,5,5-tetrakis(difluoramino)hexane <u>is shown in Figure 2.</u>

*
Aerojet-General Report No. 0235-01-10, 14 April 1961, Fig. 7 (Confidential).

CONFIDENTIAL

II Technical Discussion, A (cont.)   Report No. 0235-01-14

b.   Ethyl 5,5-bis(Difluoramino)hexanoate

To a refluxing solution of about 7 g of difluoramine in 15 cc of concentrated sulfuric acid, 1.58 g (0.01 mole) of distilled ethyl 5-keto-hexoate was added during 15 min at -10°C to 3°C. This solution was then transferred to a glass pressure bomb containing 30 ml of 20% fuming sulfuric acid at -80°C. The bomb was sealed and the -80°C bath was removed. After a reaction period of 50 hr at ambient temperature, the homogeneous acid solution was quenched over 200 cc of crushed ice, and a water-insoluble liquid separated. The mixture was extracted with five 50-ml portions of methylene chloride, and the combined extracts were washed with distilled water to pH-5. The organic solution was dried 24 hr over sodium sulfate, and the solvent was removed under reduced pressure to yield 1.6 g of a yellow liquid. Vacuum distillation gave 0.8 g of colorless liquid, bp 90 to 93°C/1.9 to 2 mm. Analysis by capillary gas chromatography indicated that the product was 96% pure, containing 4% ethyl 5-ketohexanoate.

Anal.Calcd. for $C_8H_{14}O_2N_2F_4$: C, 39.02; H, 5.73; N, 11.38; F, 30.86. Calcd. for $(C_8H_{14}O_2N_2O_4 + 4\% C_8H_{14}O_3)$: C, 39.88; H, 5.85; N, 10.92; F, 30.43. Found: C, 39.7; H, 5.68; N, 10.8; F, 31.5.

c.   Reaction of Methyl Levulinate with Difluoramine

Approximately 8 g of difluoramine was condensed into a glass pressure reactor containing 45 ml of 100% sulfuric acid and 3.0 g of methyl levulinate. The reaction was allowed to proceed at ambient temperature for 36 hr, and was then quenched with 200 ml of crushed ice. The product was extracted with methylene chloride, washed with water and dried over sodium sulfate. Removal of the solvent left 0.8 g of yellow liquid. Preparative gas chromatography gave two components, 60% and 40% respectively, which were identified by their infrared spectra as methyl levulinate and 4-(difluoramino)-γ-valerolactone.

d.   Cyclohexyldifluoramine

(1)   Cyclohexene (2.15 g, 0.025 mole) was added dropwise during 45 min to a refluxing mixture of 7 g of difluoramine and 15 ml of concentrated sulfuric acid. The reaction temperature was maintained at -15 to -25°C

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II Technical Discussion, A (cont.)   Report No. 0235-01-14

by means of a dry ice-acetone bath. When the addition was completed, the reaction was immediately quenched by pouring over 200 ml of crushed ice. The product was extracted with three 50-ml portions of methylene chloride, and the combined extracts were washed with 50 ml of water and dried over sodium sulfate. The solvent was distilled off using a 6-in. packed column, and the residue was vacuum distilled without a column to yield 0.6 g of colorless liquid, bp $38°C/25$ mm; n_D^{24} 1.4175. Gas chromatography showed 6 minor impurities, with the major component comprising 92% of the sample. An analytical sample was separated by gas chromatography.

<u>Anal</u>.Calcd. for $C_6H_{11}NF_2$: C, 53.3; H, 8.15; N, 10.37. Found: C, 53.0 H, 7.90: N, 10.4.

The yield of pure cyclohexydifluoramine was 16.3%.

(2) Cyclohexene (5 g, 0.061 mole) was added dropwise to a refluxing mixture of about 8 g of difluoramine and 15 ml of methanesulfonic acid. The temperature was maintained below $10°C$ during the addition. Fifteen min after the addition was completed, the difluoramine and product were condensed in a $-80°C$ trap at 5 mm. Removal of the difluoramine using a nitrogen sweep left 1.0 g (12.2% yield) of cyclohexyldifluoramine, identified by its infrared spectrum.

The remaining contents of the reaction flask were poured onto ice. A layer immediately settled to the bottom. This layer was extracted from the aqueous phase using methylene chloride, dried over calcium sulfate, filtered, and the solvent was distilled off. The liquid residue was distilled to yield 3.19 g of colorless liquid, n_D^{25} 1.4648, bp $75-80°C/0.3-0.4$ mm. The infrared spectrum showed absorption peaks at 7.4 and 8.1 μ ($0-SO_2-$).

<u>Anal</u>.Calcd. for $C_7H_{14}O_3S$ (cyclohexyl methanesulfonate): C, 47.20; H, 7.87. Found: C, 47.30; H, 7.92.

Approximately 7 g of difluoramine was allowed to reflux over 7.1 g (0.04 mole) of cyclohexyl methanesulfonate. There was no visual evidence of reaction. Methanesulfonic acid (0.3 ml) was then added and the mixture was allowed to reflux for 2 hr. Quenching the solution with ice, followed by extraction with methylene chloride and distillation, yielded 6.3 g (90% recovery) of cyclohexyl methanesulfonate, and no cyclohexyl difluoramine.

II Technical Discussion, A (cont.)   Report No. 0235-01-14

e.   Reaction of t-Pentyl Alcohol with Difluoramine

t-Pentyl alcohol (2.2 g, 0.025 mole) was added dropwise over a 50 min period to a refluxing mixture of 15 ml of sulfuric acid and approximately 7 g of difluoramine. It was necessary to cool the reaction flask with dry ice in order to keep the temperature below $-10^{o}C$. A layer separated during the addition. The difluoramine was refluxed until the layer dissolved (approximately 2-1/2 hours). The solution was poured over 150 ml of cracked ice. The product was extracted with three 50-ml portions of methylene chloride. The methylene chloride solution was washed with three 50-ml portions of water and dried over sodium sulfate. The bulk of the methylene chloride was distilled off through a packed column, leaving approximately 5 ml. Simple distillation of this residue gave 2.6 g, bp $40-45^{o}C$, identified by its infrared spectrum as mainly methylene chloride, and second fraction, (1.3 g) bp $50-53^{o}C$. The infrared spectrum of this fraction indicated methyl ethyl ketone and acetone, as well as hydroxyl and NF absorption.

Analysis by gas chromatography indicated that the ratio of methyl ethyl ketone to acetone was 1:3, with no peaks with a higher retention time.

f.   Ethyl N-sec-butyl-N-fluorocarbamate

Experimental ethyl-N-fluorocarbamate (4 g, 0.037 mole) was added dropwise to 30 ml of stirred concentrated sulfuric acid at 0 to $10^{o}C$. To this solution (maintained at 7 to 9°) was added with stirring 4.36 g (0.037 mole) of n-butyl nitramine over a period of 20 min. When the reaction mixture was poured onto ice, a colorless upper layer separated. The product was extracted with methylene chloride, dried over Drierite, filtered and the solvent was removed. The residue was flash distilled at 120 mm and ambient temperature to yield 2.5 g of colorless liquid, n_D^{25} 1.4068. Gas chromatography showed that the sample was chiefly one component with a minor impurity. A sample of the major component was purified by gas chromatography.

Anal. calcd. for $C_7H_{14}NO_2F$: C, 15.5; H, 8.59; N, 8.59; F, 11.67. Found: C, 51.2; H, 8.92; N, 8.62; F, 12.40.

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II Technical Discussion, A (cont.)   Report No. 0235-01-14

The 60-mc proton NMR spectrum (Figure 10) was obtained using a carbon tetrachloride solution of the sample (11.9 wt%) with tetramethylsilane added as an internal reference. The ester ethyl triplet and quartet appear at 8.67 and 5.75 (tau values) respectively. The irregular triplet centered at 9.04 is assigned to the sec-butyl $\underline{CH}_3CH_2CHCH_3$ methyl group. The complex multiplet (most intense peak 100 cps from TMS) is then assigned to the $CH_3\underline{CH}_2CHCH_3$ methylene protons. When the multiplet to the high field side of the ethyl methylene quartet at 5.75 is examined at higher RF power it is seen to be one of a pair of sextets. The other member of the pair is buried under the 5.75 quartet but several lines are resolved. This pair of sextets is assigned to the sec. butyl methine proton $-CH_2\underline{CH}(\overset{|}{N}F)CH_3$. The J_{HF} extracted is 42 cps. The spectrum is completely consistent with the structure

$$\begin{array}{c} F \\ \diagdown \\ \diagup N\text{-}CO_2Et \\ CH_3CH_2CHCH_3 \end{array}$$
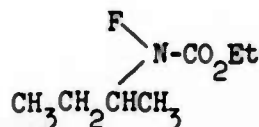
The 56.4-mc F^{19} spectrum (Figure 11) was obtained using the same sample with $CFCl_3$ added as an internal reference. The spectrum consists of two doublets; + 5510 cps from $CFCl_3$ (97.8 ppm) splitting 40 cps, and + 6679 cps (+ 118.3 ppm) splitting 56 cps. On the basis of the splitting the +5510-cps doublet is assigned to $>N\underline{F}$ in the structure obtained from the proton spectrum. No assignment is obvious for the +6679-cps doublet.

         g.   NMR Spectra of Crotonic Acid Adduct (Figures 7 and 8)

The 60-mc proton NMR spectrum was obtained in CCl_4 solution (12.2 wt%) with TMS added as an internal reference. The doublet at Tau = 8.55 (splitting approximately 7 cps) is assigned to the terminal methyl group. The nature of this signal alone eliminates the alternative structure, $CH_3CH_2CH(NF_2)CO_2H$, for which the methyl signal would be, roughly at least, a triplet. The signal at Tau = -2.20 is assigned to the carboxyl proton. The remainder of the spectrum seems to be of the ABX type (where A & B are the protons on the α-carbon and X is $-C\underline{HN}\,F_2-$) with the X portion further complicated by coupling to $-C\underline{H}_3$ and $N\underline{F}_2$. The AB portion consists of a pair of overlapping

· quartets (130, 148, 166, 183 and 138, 156, 171, 188 cps from TMS). The X portion is a very complicated multiplet centered at 239 cps from TMS. It represents the single $-C\underline{H}(NF_2)-$ proton coupled to the adjacent $C\underline{H}_3$, $-C\underline{H}_2$ (nonequivalent protons) and $N\underline{F}_2$.

The 56.4-mc F^{19} NMR spectrum was obtained with the same sample using added $CFCl_3$ as an internal reference. The spectrum consists of a doublet (splitting approximately 24 cps) centered at -2157 cps (-38.3 ppm) from internal $CFCl_3$. This splitting is assigned to the coupling with the proton on the adjacent carbon. The signals might be expected to be split further into nonequivalent quartets since the NF_2 group is attached to an assymmetric carbon but no such splitting is apparent.

B. REACTIONS OF N-FLUOROCARBAMATES (V. GRAKAUSKAS)

1. Discussion

In the previous report evidence was presented that ethyl N-flurocarbamate reacts with hot concentrated sulfuric acid to give either N-fluorosulfamic acid or N-fluoroammonium sulfate. The sulfuric acid reaction product was shown to react with n-butyraldehyde to give n-butyronitrile, which seemed to involve the fluoramine as intermediate.

The work on the identification of N-fluorocarbamate-sulfuric acid reaction product was continued. The F^{19} NMR spectrum of the material in concentrated sulfuric acid (Figure 12) showed a quadruplet which would be expected of N-fluoroammonium salt, but not of N-fluorosulfamic acid. This spectroscopic evidence in conjunction with the butyraldehyde reaction seems to support the N-fluoroammonium salt structure:

$$NHFCOOC_2H_5 \ + \ H_2SO_4 \xrightarrow{\Delta} NH_3F \overset{\oplus}{} + \ CO_2$$
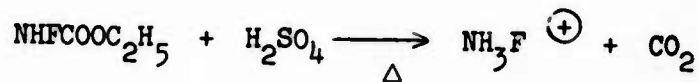
Additional evidence in favor of this structure was obtained in a reaction of aqueous cyclohexanone with the N-fluorocarbamate-sulfuric acid reaction product to yield ϵ-caprolactam. This reaction can be explained on the

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basis of the hydrolysis of N-fluoroammonium salt with the _in situ_ formation of
fluoramine. The formation of a 1:1 adduct of fluoramine and cyclohexanone followed
by a Beckmann-type rearrangement would give ϵ-caprolactam:

$$NH_3F^{\oplus} + H_2O \longrightarrow [H_2NF] + H_3O^{\oplus}$$
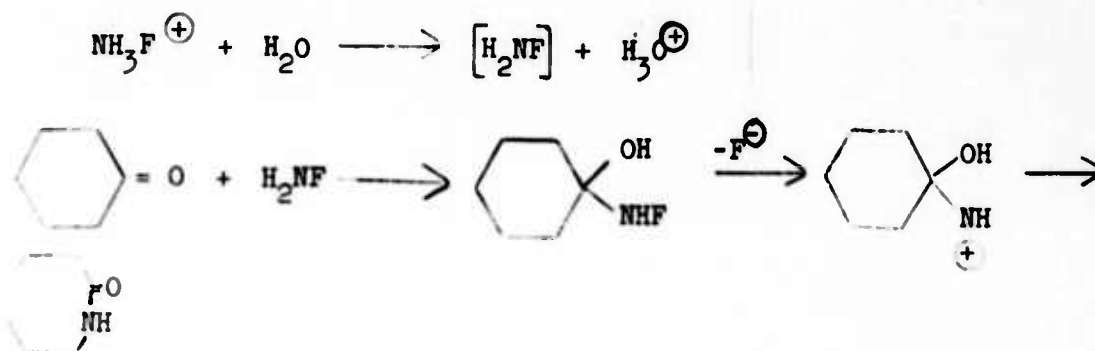
The sulfuric acid reaction was extended to ethyl N-fluoro-N-
methylcarbamate. Similarly to ethyl N-fluorocarbamate, ethyl N-fluoro-N-Methyl-
carbamate was found to be stable and soluble in concentrated sulfuric acid at
room temperature, but it decomposed with the evolution of carbon dioxide when
the solution was heated to 50-60°C. The F^{19} NMR spectrum of the resulting
sulfuric acid solution (Figure 13) showed three quadruplets, as would be expected
for the N-fluoro-methylammonium salt:*

$$CH_3NFCOOC_2H_5 + H_2SO_4 \xrightarrow{\Delta} CH_3NH_2F^{\oplus} + CO_2$$
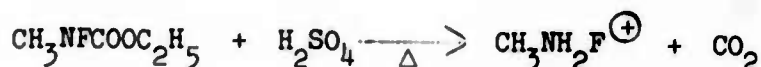
An attempt to isolate N-fluoromethylamine by diluting the
sulfuric acid solution with water was unsuccessful.

$$CH_3NH_2F^{\oplus} + H_2O \longrightarrow CH_3NHF + H_3O^{\oplus}$$

No gaseous products were evolved. The aqueous solution oxidized potassium iodide,
but the oxidizing power gradually decreased and was practically absent when the
solution was allowed to stand at room temperature for a few hours.

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*For comparison, the F^{19} NMR spectrum of ethyl N-fluorocarbamate in concentrated
sulfuric acid is shown in Figure 14.

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Reaction of the sulfuric acid hydrolysis product with aqueous cyclohexanone gave N-methyl-caprolactam. This reaction, probably involving N-fluoromethylamine formed *in situ* from its ammonium salt, is analogous to the formation of ϵ-caprolactam discussed above:

$$CH_3NH_2F^{\oplus} + H_2O \longrightarrow [CH_3NHF] + H_3O^{\oplus}$$
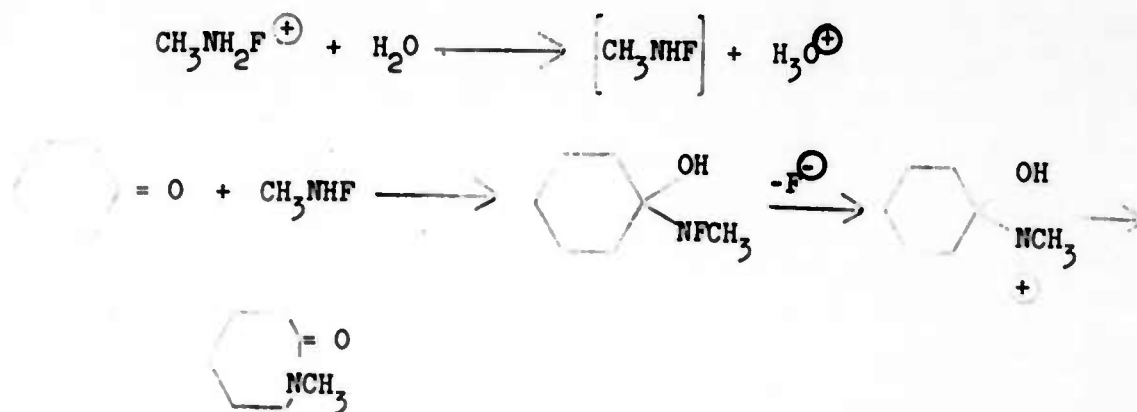
Several unsuccessful attempts have been made to isolate N-fluoro-ammonium salts. When the concentrated sulfuric acid solution of the hydrolysis product of ethyl N-fluorocarbamate was diluted with ether, absolute ethanol, or a mixture of these solvents, a white solid was deposited. This solid oxidized potassium iodide. Its infrared spectrum was identical with that of ammonium sulfate. The material analyzed for 4-12% fluorine and 18-21% nitrogen, with large variations from batch to batch.

Calcd. for N-fluoroammonium sulfate: F, 22.6%; N, 16.7%.

Ethyl N-fluorocarbamate also reacted with 72% perchloric acid at 45-60°C with the evolution of carbon dioxide, and subsequently, silicon tetra-fluoride. Some white solid deposited either on cooling or on dilution of the perchloric acid solution with ethanol. The solid oxidized potassium iodide and its infrared spectrum was identical with that of ammonium perchlorate. The material contained only 4% fluorine.

One attempt to hydrolyze ethyl N-fluorocarbamate in refluxing trifluoroacetic acid failed, and unreacted starting materials were recovered. Efforts to isolate N-fluoroammonium salts are continuing.
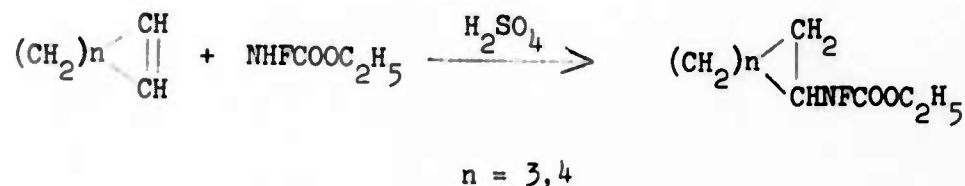
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The ethyl N-fluorocarbamate is obtained on direct fluorination of aqueous ethyl carbamate, and the material is separated from urethane by a tedious fractional distillation. In searching for an improved purification technique, conversion of ethyl N-fluorocarbamate to its salts was considered. The sodium salt of ethyl N-fluorocarbamate has been reported* to be stable in methanolic solution at ambient temperatures for several weeks and it was intended to utilize this reaction to separate the N-fluorocarbamate from carbamate. The ethyl N-fluorocarbamate was dissolved in methanolic sodium methoxide at $0-5^{\circ}$C. However, as soon as the cooling bath was removed, the temperature of the solution rose to the boiling point of methanol. In another experiment, the reaction with sodium methoxide was carried out in a mixture of methanol and diethyl ether. The reaction temperature was kept at $7-15^{\circ}$C with a 0°C bath. Sodium fluoride was isolated quantitatively from the reaction mixture, and the ethyl methyl ester of iminodicarboxylic acid, $CH_3OOCNHCOOC_2H_5$, was identified as one of the organic products.

The study of the reactions of ethyl N-fluorocarbamate with unsaturated compounds was continued. Ethyl N-fluorocarbamate was added to cyclohexene and cyclopentene in concentrated sulfuric acid:

$$(CH_2)n\overset{CH}{\underset{CH}{\|}} + NHFCOOC_2H_5 \xrightarrow{H_2SO_4} (CH_2)n\overset{CH_2}{\underset{CHNFCOOC_2H_5}{|}}$$

$$n = 3, 4$$

The structures of the adducts were confirmed by elemental analysis and infrared (Figures 15 and 16) and NMR spectra (Figures 17 through 20). In the cyclopentene reaction a side product, tentatively identified as ethyl bis(cyclopentyl)carbamate was also obtained.

Ethyl N-fluoro-N-methylcarbamate was reacted with 100% nitric acid with the expectation that it might form methyl N-fluoroammonium nitrate which could be obtained as a solid by removal of the excess of nitric acid. A reaction

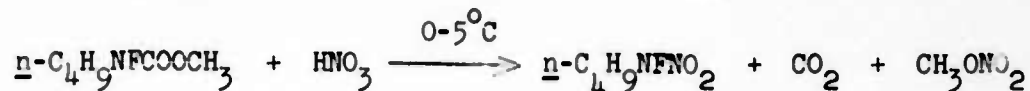*Rohm & Haas Report No. P-61-2, April 1 - June 30, 1961 (Confidential).

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occurred at 0-5°C and carbon dioxide was evolved. The product, however, was found to be a mixture of two volatile liquids which could not be readily separated by distillation. This separation problem was avoided by substituting the methyl for the ethyl ester. In this case, N-fluoro-N-$\underline{n}$-butylamine was obtained in 65-70% yield.

$$\underline{n}\text{-}C_4H_9NFCOOCH_3 + HNO_3 \xrightarrow{0\text{-}5°C} \underline{n}\text{-}C_4H_9NFNO_2 + CO_2 + CH_3ONO_2$$

This compound has been previously prepared by the direct fluorination of the aqueous potassium salt of $\underline{n}$-butylnitramine.*

$$\underline{n}\text{-}C_4H_9NNO_2^{\ominus}K^{\oplus} + F_2 \xrightarrow{(H_2C)} \underline{n}\text{-}C_4H_9NFNO_2 + KF$$
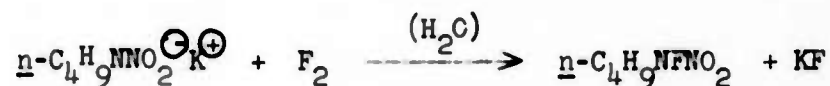
The infrared spectrum of the product (Figure 21) was identical to that of the compound obtained on direct fluorination of $\underline{n}$-butylnitramine. The F^{19} and proton (Figures 22 and 23) NMR spectra not previously reported are consistent with the structure. The nitration of N-fluorocarbamates by 100% nitric acid is probably a general reaction for the preparation of N-fluoro-N-nitramines and will be extended to poly-N-fluorocarbamates previously prepared, i.e. $CH_2(NFCOOC_2H_5)_2$, $NF_2CH_2CH_2NFCOOC_2H_5$, etc.

     2.   Experimental

         a.   NMR Spectrum of N-fluoroammonium Salt

            A solution of 6.42 g of ethyl N-fluorocarbamate (0.06 mole) in 20 ml of concentrated sulfuric acid was heated gradually to 85-95°C and kept at this temperature until the evolution of carbon dioxide ceased (20 min). After the resulting sulfuric acid solution was cooled to room temperature, the 56.4 mc F^{19} NMR spectrum (Figure 12) was obtained using a capillary containing trifluoroacetic acid as a reference. The spectrum consists of a single signal, a poorly resolved but apparently regular quartet centered at +2076 cps (+36.8 ppm)

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*Aerojet-General Report 0235-01-7, 15 July 1960 (Confidential).

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from trifluoroacetic acid with a splitting of 38 cps. It proved impossible to record spectra while spinning the sample (presumably an effect of the high sample viscosity) which accounts at least in part for the poor resolution.

The 56.4-mc F^{19} NMR spectrum (Figure 14) of ethyl N-fluoro-carbamate in concentrated sulfuric acid (10% solution) was obtained using trifluoroacetic acid as an external reference. The sample was not spun. The spectrum consists of a single, somewhat broadened signal at +1549 cps (+27.5 ppm) from trifluoroacetic acid. On the basis of the expected structure $\overset{+}{N}H_2FCOOC_2H_5$ the signal should be a triplet (split by $\underline{N}H_2$). The signal is somewhat broadened but no splitting is observed. This may be an effect of rapid proton exchange between H_2SO_4 and $\overset{+}{N}H_2FCOOC_2H_5$. Such an exchange may also explain the poor resolution of the quartet F^{19} resonance observed in $NH_3F^{\pm}$ (see Figure 12).

b.   NMR Spectrum of Methyl N-fluoroammonium Salt

A solution of 6.0 g ethyl N-fluoro-N-methylcarbamate (0.05 mole) in 20 ml of concentrated sulfuric acid was heated at 85-95°C until the evolution of carbon dioxide ceased (20 min) and was then cooled to room temperature. The 56.4-mc F^{19} NMR spectrum (Figure 13) was obtained using trifluoroacetic acid as an external reference. The sample was not spun. The spectrum consists of a single signal, a multiplet centered at -1664 cps (-29.5 ppm) from trifluoroacetic acid. When examined at low sweep speeds this multiplet appears to be an incompletely resolved triplet of quartets. Eleven peaks and/or shoulders can be picked out. The spacings extracted are for the triplet 42 cps and for the quartets 28 cps.

The spectrum is consistent with the structure $CH_3NH_2F^{\oplus}$, the fluorine signal being split into a triplet by the $\underline{N}H_2$ (J=42 cps) and the components of the triplet being split further into quartets by the $C\underline{H}_3$ protons (J=28 cps). The other possible structure, CH_3NFSO_3H appears to be ruled out as it would be expected to give a quartet whose components would be split slightly, if at all, by the comparatively remote proton.

The chemical shift of the $CH_3NH_2F^{\oplus}$ multiplet relative to Freon-11, obtained **approximately** by substracting the shift relative to trifluoroacetic acid from the shift of trifluoroacetic acid relative to Freon-11, i.e. 4430-1664 cps, is +2766 cps or +49.1 ppm from Freon-11.

c.   Reaction of N-fluoroammonium Salt with Cyclohexanone

A solution of 6.4 g (0.06 mole) of ethyl N-fluorocarbamate in 30 ml of concentrated sulfuric acid was heated at 85-95°C until the evolution of carbon dioxide ceased. The resulting solution was cooled to 0-5°C and poured on a mixture of 130 g of crushed ice and 4.9 g (0.05 mole) cyclohexanone. The mixture was allowed to stand at room temperature for five hours. The mixture was then neutralized with sodium hydroxide and extracted with five 50-ml portions of diethyl ether. The dried and filtered ethereal solution was concentrated and the residual solid, 2.5 g, was recrystallized from n-pentane to give 2.0 g of white crystalline solid, mp 68°C, alone or when mixed with an authentic sample of ε-caprolactam. The infrared spectrum of the product was identical to that of ε-caprolactam. The yield based on ethyl N-fluorocarbamate was 30%. In another experiment the N-fluorocarbamate-sulfuric acid reaction was carried out in the same manner. The solution was cooled and to it was added at 0-2°C with stirring 4.9 g (0.05 mole) of cyclohexanone over a period of 25 min. The resulting mixture was stirred at 5-10°C for 30 min, and then poured onto 70 g of crushed ice. From the aqueous solution 3.5 g of ε-caprolactam (50% yield) was isolated.

d.   Reaction of N-fluoromethylammonium Salt with Cyclohexanone

A solution of 6.1 g (0.05 mole) of ethyl N-fluoro-N-methyl-carbamate in 30 ml of concentrated sulfuric acid was heated at 85-95°C until the evolution of carbon dioxide ceased (20 min). The solution was cooled to 0-5°C and poured on a mixture of 150 g of crushed ice and 4.4 g (0.045 mole) of cyclohexanone. The resulting solution was allowed to stand at room temperature for 4 hours and then was extracted with four 25-ml portions of methylene chloride. The combined extracts were dried with Drierite, filtered, and concentrated. The residual liquid was distilled to give 2.5 g of a colorless liquid, bp 47-50°C/ 0.1-

0.3 mm, n_D^{25} 1.4814, which was identified as N-methylcaprolactam (reported* bp 120°C/19 mm, n_D^{25} 1.4818). The infrared spectrum was also consistent with this structure. The yield based on ethyl N-fluoro-N-methylcarbamate was 30%.

e. Attempted Isolation of N-fluoroammonium Sulfate

A solution of 5.4 g (0.05 mole) of ethyl N-fluorocarbamate in 20 ml of concentrated sulfuric acid was heated at 85-95°C until the evolution of carbon dioxide ceased (20 min), cooled to room temperature, and added dropwise with stirring and cooling (10-15°C) to 80 ml of absolute ethanol. The clear solution was allowed to stand at room temperature overnight resulting in a deposition of a white solid. The solid was collected by filtration under nitrogen, and was washed with five 10-ml portions of absolute ethanol, and five 15-ml portions of diethyl ether. The solid was dried in a vacuum desiccator at 0.1 mm, and amounted to 2.5 g. It oxidized potassium iodide, and melted with decomposition at 220-240°C.

Anal. Calcd. for $NH_3F^{\oplus}$ $HSO_4^{\ominus}$: N, 10.52; F, 14.27. Calcd. for $(NH_3F)_2SO_4$: N, 16.7; F, 22.6. Found: N, 17.8; F, 9.8.

In another experiment, the sulfuric acid solution was added to absolute ethanol in the same manner as described above. The resulting solution was then added with stirring to 100 ml of anhydrous diethyl ether. The white solid deposited in a matter of three hours. The solid analyzed as 4.8% fluorine and 20% nitrogen.

f. Attempted Preparation of N-fluoroammonium Perchlorate

Ethyl N-fluorocarbamate, 4.3 g (0.04 mole), was added at 0.5°C with vigorous stirring to 10 ml of 72% perchloric acid. The reaction flask was connected in series with an evacuated infrared gas cell allowing samples of gaseous reaction products to be taken. The solution was heated gradually, and at 45-55°C gas evolution began. The gaseous product was found by its infrared spectrum to be pure carbon dioxide.

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R. E. Benson and T. L. Coirs, J. Am. Chem. Soc., 70, 2115 (1948).

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The reaction mixture was heated at 60-65°C for 75 min. Another gas sample was taken, which showed carbon dioxide contaminated with silicon tetrafluoride.

At the end of 75 min heating at 60-65°C the evolution of gas was very slow and the reaction mixture was cooled to 0-5°C, resulting in a deposition of a white solid. The solid was collected by filtration (nitrogen atmosphere), and washed with five 20-ml portions of absolute ethanol, followed by five 30-ml portions of diethyl ether. The material, dried at 0.1 mm, amounted to 1.3 g. It oxidized potassium iodide, and did not melt at 300°C. Its infrared spectrum was identical with that of ammonium perchlorate.

$\underline{Anal}$. Calcd. for NH_3FClO_4: F, 14%. Found: F, 4.3%.

h.   Decomposition of Ethyl N-fluorocarbamate with Methanolic Sodium Methoxide

Methanolic sodium methoxide solution was prepared by dissolving 1.15 g of metallic sodium in 25 ml of dry methanol. To this solution was added dropwise with stirring at 0-3°C, 5.4 g (0.05 mole) of ethyl N-fluoro-carbamate over a period of ten min. The reaction was exothermic, but the temperature could be kept at 0-3°C by means of an ice-water cooling bath. At the end of the addition the cooling bath was removed and in a matter of few minutes the reaction mixture heated up to the boiling point of methanol.

The reaction was repeated with the same quantities of starting materials, except that methanolic sodium methoxide solution was diluted with 25 ml of anhydrous diethyl ether before addition of the N-fluorocarbamate. Again, the reaction became highly exothermic, but the temperature could be kept at 7-15°C. The reaction was completed in 10-15 min at this temperature. At the end of the run the reaction mixture was allowed to warm up to room temperature and the solvents were removed at reduced pressure. The viscous residual oil on treatment with 50 ml of methylene chloride deposited a white solid. This solid was removed by filtration, washed with methylene chloride and dried; it was identified as sodium fluoride; wt 2.0 g.

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The methylene chloride solution was concentrated to remove the solvent and the residual oil was distilled. After removal of $\underline{ca}$. one ml of an unidentified liquid, bp 25-29°C/0.1-0.3 mm, a semisolid residue remained. This material was crystallized from $\underline{n}$-pentane to give 0.7 g of a white microcrystalline solid, mp 64°C, which was identified as methyl ethyl ester of iminodicarboxylic acid.

$\underline{Anal}$.Calcd. for $C_5H_9NO_4$; C, 40.82; H, 6.17; N, 9.5. Found C, 41.10; H, 6.06; N, 9.7.

g.   Ethyl N-Cyclohexyl-N-Fluorocarbamate

To a solution of 4.3 g (0.04 mole) of ethyl N-fluoro-carbamate in 22 ml concentrated sulfuric acid at 0-5°C was added with cooling and vigorous stirring 3.3 g (0.04 mole) of cyclohexene over a period of 5-7 min. At the end of the addition the cooling bath was removed and the yellow solution was allowed to warm up by itself. The reaction temperature increased gradually to 28°C. After standing at this temperature for 10-15 min, the reaction mixture cooled to 24-5°C. The reaction mixture was stirred at 24-45°C for 30 min, then cooled to 0-5°C and poured on 80 g of crushed ice. The dark oily liquid was extracted with four 20-ml portions of methylene chloride, the combined extracts dried with Drierite, filtered and the filtrate concentrated to remove the solvent. The dark residual liquid was purified by distillation to give 6.2 g of a colorless liquid, bp 50-51°C/0.1 mm, n_D^{25} 1.4430. Yield was 82%.

Some of the material was redistilled for analyses; bp and n_D^{25} same as above.

$\underline{Anal}$.Calcd. for $C_9H_{16}NFO_2$: C, 57.12; H, 8.52; N, 7.40; F, 10.0. Found: C, 56.7; H, 8.65; N, 7.65; F, 10.5.

The infrared spectrum (Figure 16) is consistent with ethyl N-cyclohexyl-N-fluoro-carbamate structure.

The proton (Figure 20) and F^{19} (Figure 18) NMR spectra were obtained in carbon tetrachloride solution with TMS and Freon-11 as internal references. Proton chemical shifts are expressed as tau values. Proton Spectrum:

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The ester ethyl triplet and quartet appear at 8.74 and 5.84, respectively. The triplet is superimposed on a broad unresolved signal (peak at 8.29) which is assigned to the cyclohexyl ring protons. The signal is broadened, presumably, due to a rapid inversion of the ring. Two broad weak signals at 6.56 and 5.94 (under the ethyl group quartet) may be assigned to the proton at the substituted ring position (split by the adjacent ring protons + N$\underline{F}$). F^{19} Spectrum: The F^{19} spectrum consists of a doublet at +92.1 ppm from internal Freon-11. It is assigned to RN$\underline{F}$COOEt (split by the proton on the adjacent cyclic carbon).

h.   Ethyl N-Cyclopentyl-N-fluorocarbamate

Reaction between ethyl N-fluorocarbamate, 6.43 g (0.06 mole), and cyclopentene, 4.1 g (0.06 mole), in 30 ml of concentrated sulfuric acid was carried out in an identical manner as that described above for cyclohexene. The reaction product was purified by distillation to give 3.5 g of a colorless liquid, bp 39°C/0.2 mm, n_D^{25} 1.4375 (34% yield), which was identified as ethyl N-cyclopentyl-N-fluorocarbamate.

<u>Anal</u>. Calcd. for $C_9H_{14}NFO_2$: C, 54.84; H, 8.05; N, 8.00; F, 10.84. Found: C, 54.40; H, 7.99; N, 8.21; F, 12.3.

After removal of the N-fluorocarbamate adduct, the residual dark liquid was distilled to give 2.3 g of a colorless liquid, bp $83-98^{\circ}$C/0.2 mm, n_D^{25} 1.4750. This material was redistilled and a middle cut, 1.5 g bp $86-7^{\circ}$C/0.2 mm, n_D^{25} 1.4765, was taken for analyses. On the basis of its infrared spectrum and elemental analysis, the material was tentatively identified as contaminated ethyl dicyclopentylcarbamate.

<u>Anal</u>.Calcd. for $C_{13}H_{23}NO_2$: C, 69.9; H, 9.48; N, 6.3. Found: C, 68.1; H, 9.79; N, 6.34.

The infrared spectrum of ethyl N-cyclopentyl-N-fluorocarbamate is shown in Figure 15.

The 60-mc proton NMR spectrum (Figure 19) of ethyl N-cyclopentyl-N-fluorocarbamate was obtained in carbon tetrachloride solution with added TMS as an internal reference. The triplet-quartet of the ester ethyl group appears at 8.67 and 5.75 (tau values). The partially resolved multiplet

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(peak at -105 cps from TMS) may be assigned to the cyclopentyl ring protons. Two weak multiplets appeared at 5.15 and 5.85 (estimated), the latter under the ethyl group quartet. When these are examined at a higher r-f intensity, they are seen to be irregular quintets, and thus the signals may be assigned to the proton on the -NFCOOEt substituted carbon (split by adjacent $\underline{H}C_2$ and $N\underline{F}$). The spectrum is therefore consistent with the proposed structure. The 56.4-mc F^{19} NMR spectrum (Figure 17) was obtained using carbon tetrachloride solution, to which Freon-11 was added as an internal reference. The spectrum consists of a single signal, a doublet (splitting approximately 44 cps) centered at +5055 cps (+89.7 ppms) from Freon-11. The signal is assigned to $>CHN\underline{F}COOC_2H_5$ and the F^{19} spectrum is consistent with the proposed structure.

i.   Nitration of Methyl N-n-Butyl-N-fluorocarbamate

Methyl N-n-butyl-N-fluorocarbamate required for this reaction was prepared by direct fluorination of aqueous methyl N-butylcarbamate as previously described.*

To 25 ml of 100% nitric acid at -5 to 0°C was added dropwise, with cooling and vigorous stirring, 4.0 g methyl N-n-butyl-N-fluorocarbamate over a period of 30 min. A vigorous gas evolution occurred during the addition and the gas was found by its infrared spectrum to be carbon dioxide containing a small amount of silicon tetrafluoride. At the end of the addition of the N-fluorocarbamate, the reaction mixture was stirred for an additional 15 min at -5 to 0°C, and then poured on 100 g of crushed ice. The water-insoluble liquid was extracted with two 20-ml portions of methylene chloride and the combined extracts dried with Drierite. At the end of the drying period, 2-3 g of sodium bicarbonate was added to the mixture to remove traces of nitric and/or hydrofluoric acid. The filtered solution was concentrated to remove the solvent and the residual liquid distilled to give 2.5 g of a colorless liquid, bp 40-41°C/25-28 mm, n_D^{25} 1.4040. This

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* Aerojet-General Report No. 1960, February 1961, p. 28, Contract No. AF49(638)-838 (Confidential).

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material was identified as N-fluoro-N-nitro-n-butylamine (65% yield) by com-
paring its infrared spectrum (Figure 21) and physical properties with those of
a known compound previously prepared by direct fluorination of n-butyl-nitramine
salt.*

Anal. Calcd.for $C_4H_9N_2FO_2$: C, 35.29; H, 6.66; N, 20.58. Found: C, 34.86;
H, 6.21; N, 20.2.

In another similar experiment, it was found that at -20 to
$-15°C$, methyl N-n-butyl-N-fluorocarbamate does not react at all or the rate of
nitration is very slow in 100% nitric acid. The evolution of carbon dioxide
seems to begin at -12 to $-9°C$. The yield of N-fluoro-N-nitro-n-butylamine was
about the same when the nitration was carried out at $-10°C$.

F^{19} NMR and proton spectra of N-fluoro-N-nitro-n-butylamine
not previously reported are shown in Figures 22 and 23, respectively.

The 60-mc proton NMR spectrum was obtained in carbon
tetrachloride solution (14.7 wt%), with TMS added as an internal standard. The
assignments are as follows. The multiplet (most intense peak 59 cps from TMS)
is assigned to the terminal methyl $CH_3CH_2CH_2CH_2-$, the multiplet with its most
intense peak 97 cps from TMS is assigned to the internal methylene protons
$CH_3\underline{CH}_2\underline{CH}_2CH_2-$, and finally the pair of triplets centered on 8 tau = 6.07 is
assigned to the α-methylene (split 35 cps by the adjacent N$\underline{F}$, and approximately
11 cps by the adjacent $\underline{CH}_2$).

The 56.4-cps F^{19} NMR spectrum was obtained with the
same solution after adding enough sample to approximate double concentration
and added Freon-11 as an internal standard. The spectrum consists of a single
signal, a triplet at -62 cps (-1.10 ppm) from Freon-11, with a splitting of
33 cps. It is assigned to $-CH_2N\underline{F}NO_2$.

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*Aerojet-General Report 0235-01-7, 15 July 1960 (Confidential).

II Technical Discussion (cont.)   Report No. 0235-01-14

C. FLUORINATION STUDIES (V. GRAKAUSKAS)

1. Discussion

It was shown previously* that N-methyl amides undergo direct fluorination to give methyldifluoramine:

$$RCONHCH_3 + F_2 \longrightarrow RCOOH + CH_3NF_2$$

Attempts to extend the above reaction to higher alkyl amides, however, resulted in the formation of a mixture of CF and NF amines. The fluorination of cyclic amides is presently under investigation with the objective of synthesizing N-fluorolactams or ω-difluoraminocarboxylic acids:

$$(CH_2)n \begin{matrix} C = 0 \\ | \\ NH \end{matrix} + F_2 \xrightarrow{H_2O} (CH_2)n \begin{matrix} C = 0 \\ \\ NF \end{matrix} \quad or \quad NF_2(CH_2)nCOOH$$
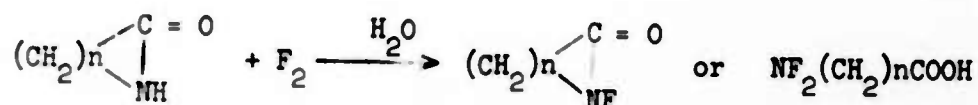
Fluorination of aqueous caprolactam gave a low-boiling mobile liquid and a viscous high-boiling oil. The structure of the low-boiling product, obtained in low yields, has not yet been definitely established. Its infrared spectrum showing the absence of OH or NH and a strong absorption bond at 5.45 μ, agrees with the structure, N-fluorocaprolactam. Preparation of N-chloro- and N-bromocaprolactams has been recently reported.** Beyer and Körösi on bromination of caprolactam isolated perbromocaprolactam, which on treatment with base yielded N-bromocaprolactam:

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*Aerojet-General Report 0235-01-10, 14 April 1961, p. 15 (Confidential).

**B. Taub and J. B. Hino, J. Org. Chem., 25, 263 (1960).
H. Beyer and J. Körösi, Ber. 94, 480 (1961).

An analogous salt was not isolated on fluorination of caprolactam. The main reaction product was identified as 6-difluoraminohexanoic acid, isolated in 50% yield. The structure was assigned on the basis of its infrared spectrum (Figure 24) and F^{19} (Figure 25) and proton (Figure 26) NMR spectra; the elemental analysis was only in a fair agreement with the structure. The material apparently underwent some decomposition on distillation. The crude material was purified by dissolving it in aqueous sodium bicarbonate and recovering it on acidification. Aqueous sodium hydroxide, however, decomposed the difluoramino acid at 0-5°C to 5-cyano-pentanoic acid.

The crude 6-difluoraminohexanoic acid was esterified in refluxing ethanol in the presence of a catalytic amount of sulfuric acid. The F^{19} (Figure 27) and proton (Figure 28) NMR and infrared (Figure 29) spectra support the ester structure, although the elemental analysis is in only fair agreement.

The fluorination of caprolactam and reactions of 6-difluoramino-hexanoic acid are summarized by the following equations:
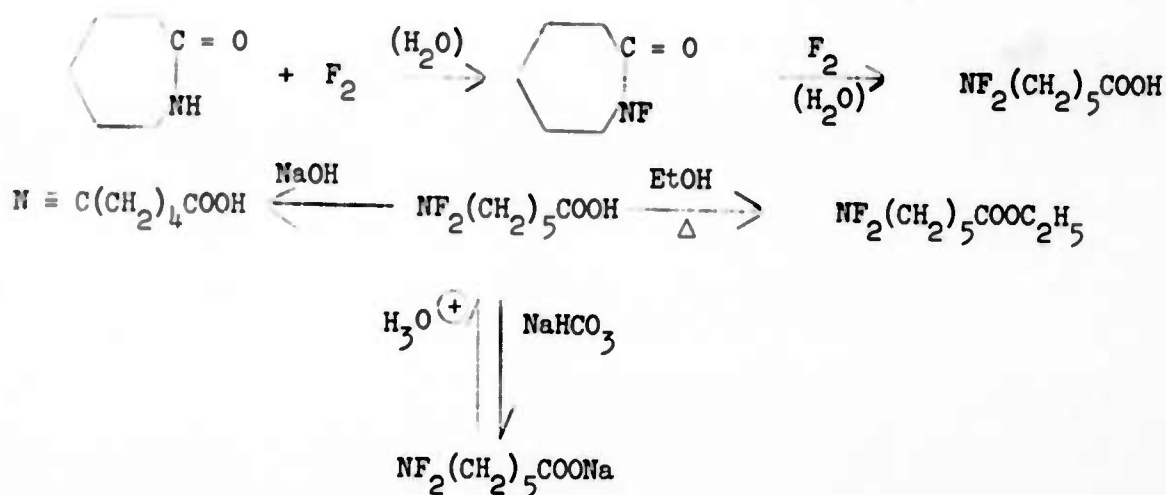
The study of the fluorination of other cyclic lactams is presently in progress.

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II Technical Discussion, C (cont.)   Report No. 0235-01-14

Direct fluorination of the cyclohexene N-fluorocarbamate
adduct gave difluoraminocyclohexane in 20% yield:
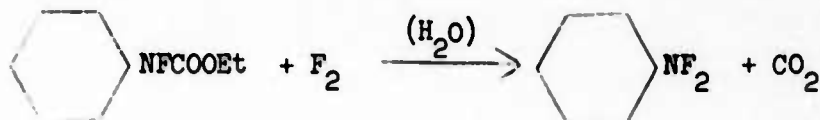
The infrared spectrum and physical properties of the material were identical with
those of the difluoramine adduct of cyclohexene.

The main product of direct fluorination of aqueous diethyl
methylenedicarbamate was previously reported* to be ethyl difluoraminomethyl-
carbamate, $NF_2CH_2NHCOOC_2H_5$. The isomeric structure, $NHFCH_2NFCOOC_2H_5$, was also
possible. The F^{19} (Figure 30) and proton (Figure 31) NMR spectra have now
confirmed the former structure.

    2.   **Experimental**

        a.   Fluorination of ϵ-Caprolactam

            (1)   <u>Preparation of 6-Difluoraminohexanoic Acid</u>

Fluorine, diluted with nitrogen (1:4), was passed at
0-5°C into a vigorously stirred solution of 56.5 g (0.5 mole) ϵ-caprolactam in
650 ml of water. The fluorination was continued until 1.0 mole of fluorine was
consumed. At the end of the run the heavy, water-insoluble oil was separated in
a separatory funnel, and the organic layer washed with three 50-ml portions of
ice water. The material, amounting to 28 g, was dissolved in 50 ml of methylene
chloride and dried with Drierite. The filtered methylene chloride solution was
concentrated to remove the solvent and the residual pale-yellow liquid was sub-
jected to vacuum distillation. A volatile colorless liquid, 1.5 g, distilled
at 30-40°C pot temperature and condensed in a dry-ice-acetone-cooled condenser.
This liquid, n_D^{25} 1.3702, oxidized potassium iodide and showed a carbonyl absorp-
tion at 5.45 µ and no NH or OH absorption in infrared.

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* Aerojet-General Report No. 0235-01-12, December 1961 (Confidential).

The residual pale-yellow oil, 25 g, n_D^{25} 1.4250, could not be distilled without decomposition. A sample of the material (3.0 g) was dissolved at room temperature in 10% aqueous sodium bicarbonate, and the solution was extracted with diethyl ether. The aqueous solution was acidified with sulfuric acid and extracted with two 20-ml portions of methylene chloride. The combined extracts were dried with Drierite, filtered and concentrated to remove the solvent. The infrared spectrum (Figure 24) and refractive index of the pale-yellow residual oil (2.6 g) were identical to those of the untreated material. This material was identified as 6-difluoraminohexanoic acid on the basis of its infrared and NMR spectra. The elemental analysis indicated that the material was somewhat impure.

<u>Anal</u>. Calcd. for $C_6H_{11}NF_2O_2$: C, 43.1; H, 6.63; N, 8.4; F, 22.7. Found: C, 44.0; H, 6.24; N, 8.3; F, 20.6.

The F^{19} (Figure 25) and proton (Figure 26) NMR spectra are consistent with the above structure.

The 60-mc proton NMR spectrum was obtained using carbon tetrachloride solution (approximately 10 wt%) with TMS added as an internal reference. The assignments are as follows: the complex multiplets (most intense peaks 105 and 144 cps from TMS are assigned to the "internal" methylene groups, $NF_2CH_2(C\underline{H}_2)_4COOH$. The three irregular triplets (182, 211, 243 cps from TMS, splitting 29, 32 cps) are assigned to the methylene to which the $-NF_2$ group is attached. The somewhat broadened peak at 733 cps (12.20 ppm) is assigned to $-COO\underline{H}$. No assignment is obvious for the two weak multiplets to the low-field side of the triplets. Presumably they are due to an impurity.

The 56.4-mc F^{19} NMR spectrum was obtained using the same carbon tetrachloride solution with Freon-11 added. The spectrum consists of a triplet of doublets (-3105, 3112; -3135, -3142; -3165, -3172 cps from Freon-11) centered at -3139 cps from Freon-11 (-55.7 ppm). By virtue of the chemical shift and the triplet splitting (30 cps), the signal may be assigned to $N\underline{F}_2CH_2^-$. The source of the splitting of the components of the triplet is not obvious. It could arise if the $-NF_2$ fluorines were rendered nonequivalent in some manner.

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II Technical Discussion, C (cont.)   Report No. 0235-01-14

Additional 6-difluoraminohexanoic acid was isolated by extracting the original aqueous phase with methylene chloride. The combined extracts were dried, filtered and the solution concentrated. The residual oil, 25 g, was found by its infrared spectrum to be a mixture of ϵ-caprolactam and 6-difluoraminohexanoic acid. Fifteen g of 6-difluoraminohexanoic acid was isolated from this mixture by purification via its sodium salt.

An attempt was made to purify the crude 6-difluoraminohexanoic acid by distillation. The material distilled at 87-90°C/0.2-0.3 mm to give a colorless liquid, n_D^{25} 1.4160. Considerable amount of the dark, viscous residue remained in the distillation flask. The infrared spectrum of the distillate was identical to that of the crude material. Elemental analysis, however, showed that the distilled acid was not pure.

Anal. Found: C, 41.2; H, 6.22; N, 7.80; F, 19.60.

(2)   Esterification of 6-Difluoraminohexanoic Acid

A 3.8-g sample of impure 6-difluoraminohexanoic acid was esterified by refluxing its solution in 20 ml of absolute ethanol containing two drops of concentrated sulfuric acid. After three hours of reflux, the solution was cooled and poured onto 100 g of crushed ice. The organic layer was extracted with methylene chloride to give 1.5 g of ethyl 6-difluoramino-hexanoate, bp 49-50°C/0.2 mm, n_D^{25} 1.4060, and approximately 2 g of unesterified acid. The unesterified acid was refluxed with 20 ml of ethanol in the pressence of a few drops of concentrated sulfuric acid for 8 hours to form an additional 2.0 g of the ethyl ester. The structure of ethyl 6-difluoraminohexanoate was established on the basis of the infrared (Figure 29) and F^{19} (Figure 27) and proton (Figure 28) NMR spectra. The elemental analysis indicated that the material was somewhat impure.

Anal. Calcd. for $C_8H_{15}NF_2O_2$:   C, 49.2; H, 7.74; N, 7.17; F, 19.5. Found: C, 48.2; H, 7.2; N, 6.74; F, 19.8.

The 60-mc proton NMR spectrum was obtained using a carbon tetrachloride solution with TMS added as an internal standard. The assignments are as follows. The ester ethyl group triplet and quartet are centered

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II Technical Discussion, C (cont.)   Report No. 0235-01-14

at 1.23 ppm (74 cps) and 4.05 ppm (243 cps) from TMS. The two complex multiplets (most intense peaks 94 and 135 cps from TMS) are assigned to the "internal" methylene groups, $NF_2CH_2(CH_2)_4COOC_2H_5$. The three irregular triplets at 177, 206 and 234 cps (overlapped by ethyl quadruplet) are assigned to the methylene, to which the NF_2 group is attached, $NF_2CH_2(CH_2)_4COOC_2H_5$.

The 56.4-mc F^{19} NMR spectrum was obtained using the same carbon tetrachloride solution with Freon-11 added as an internal reference. The spectrum consists of a triplet (-3113, -3143, -3172 cps from Freon-11, splitting approximately 30 cps) centered at -3143 cps (-55.8 ppm) from Freon-11. The chemical shift and splitting indicate assignment to $NF_2(CH_2)_5COOC_2H_5$. No splitting of the triplet component, as was observed in the corresponding acid, is apparent.

b.   Dehydrofluorination of 6-Difluoraminohexanoic Acid

To a suspension of 5.0 g (0.3 mole) of 6-difluoramino-hexanoic acid in 25 ml of water at 0-3°C was added dropwise with stirring over a period of 15 min a solution of 5.0 g of sodium hydroxide in 20 ml of water. The reaction was highly exothermic, and an efficient cooling method was required. At the end of the addition of sodium hydroxide, the reaction mixture was allowed to warm up to room temperature and stirred for an additional 15 min. Then the mixture was cooled to 0-5°C and acidified with 50% sulfuric acid. The aqueous mixture was extracted with three 20-ml portions of methylene chloride, the combined extracts dried with Drierite, filtered and concentrated to remove the solvent. The residual dark oily liquid was distilled to give 2.0 g of a colorless liquid, bp 128-135°C/0.3 mm, n_D^{25} 1.4530. Its infrared spectrum and physical properties (rep.* bp 162-170°C/1 mm) indicated that the material is 5-cyanovaleric acid.

c.   Difluoraminocyclohexane

A solution (partially in suspension) of 5.2 g (0.03 mole) of ethyl N-cyclohexyl-N-fluorocarbamate in 200 ml of water was fluorinated at 0-5°C with elementary fluorine (diluted with nitrogen; 1:4) until 0.71 (0.03 mole) of fluorine was consumed. At the end of the run the reaction mixture was extracted

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*
W. Reppe et al., Ann 596, 93, 127 (1955).

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with three 20-ml portions of methylene chloride. The combined extracts were dried with Drierite, filtered and the filtrate concentrated to remove the solvent. The residual liquid was fractionated to give 1.0 g of a colorless liquid, bp $37^\circ C/22$-26 mm, n_D^{25} 1.4146, and 2.8 g of starting material, bp 51-$2^\circ C/0.1$- 0.2 mm. The low boiling liquid was identified as difluoraminocyclohexane by comparing its infrared spectrum with that of cyclohexene-difluoramine adduct.

d. NMR Spectra of Ethyl N-Difluoraminomethylcarbamate

The 56.4-mc F^{19} NMR spectrum (Figure 30) of the crude sample (88-92%) was obtained using Freon-11 as solvent and reference. The spectrum consists of a single signal, a triplet centered at 2192 cps (37.1 ppm) from Freon-11. The splitting is approximately 24 cps.

The 60-mc proton NMR spectrum (Figure 31) was obtained using the same Freon-11 solution, with TMS added as an internal reference. The ester ethyl triplet and quartet appear at 8.74 and 5.80, respectively. The triplet is overlapped by a second, weaker triplet which is presumably due to impurities. A triplet (splitting approximately 24 cps was observed in the F^{19} spectrum) of doublets (splitting approximately 7 cps) is centered at 5.07. The doublet to high field is buried under the ethyl quartet. This group of signals is assigned to the $NF_2C\underline{H}_2NH$- protons (split by $N\underline{F}_2$ and $N\underline{H}$). The broadened signal at 3.87 is assigned to the NH proton. The remaining weak signals, including those of 1.00 and 2.02, are assigned to impurities. Considering the nature of the sample (major component 88-92%), the spectrum is in good agreement with the proposed structure, $NF_2CH_2NHCOOC_2H_5$.

III. CONCLUSIONS

A.   Under forcing conditions, 1,5-diketones can be converted to tetrakis (difluoramino) derivatives.

B.   N-Fluoroammonium salts appear to be stable, at least in sulfuric acid solution.

IV. FUTURE PLANS

Investigation in the areas reported herein will be continued.

V.   PERSONNEL

The experimental synthesis work was performed by M. A. Sims, M. P. Mascari, G. L. Gable, W. T. Maurice, H. F. Shuey, V. Grakauskas, and K. Baum. Analytical support was provided by H. Nelson, K. Inouye, D. I. Matson, and H. W. Pust.
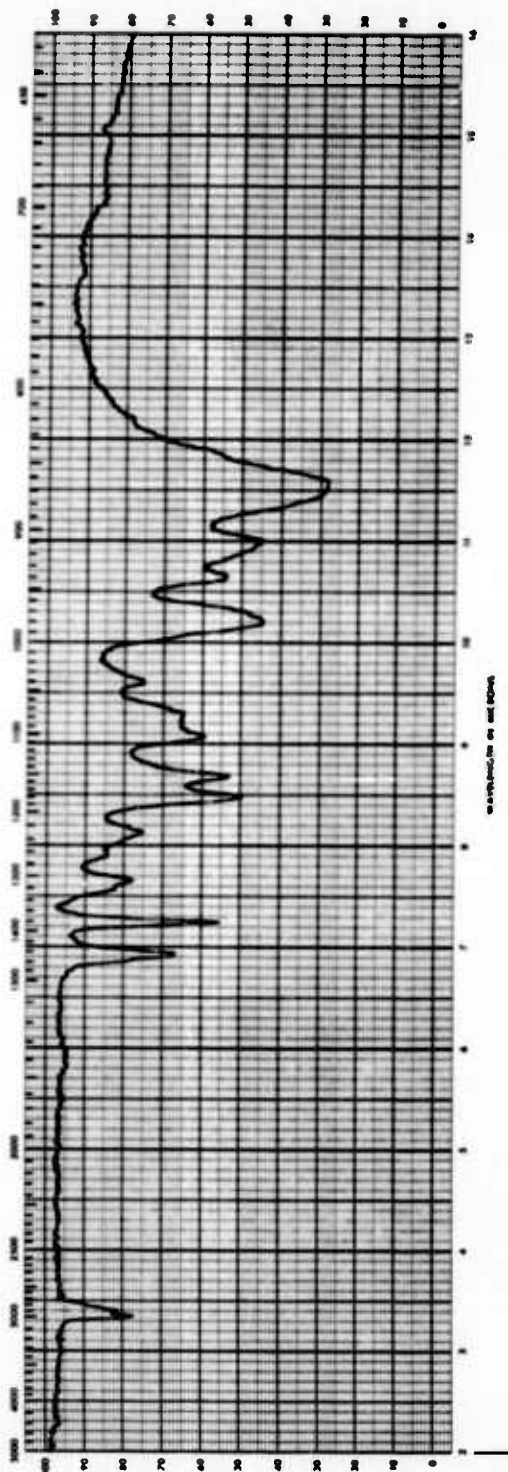
Fig. 1 Infrared Spectrum of Unknown Acetonylacetone Reaction Product
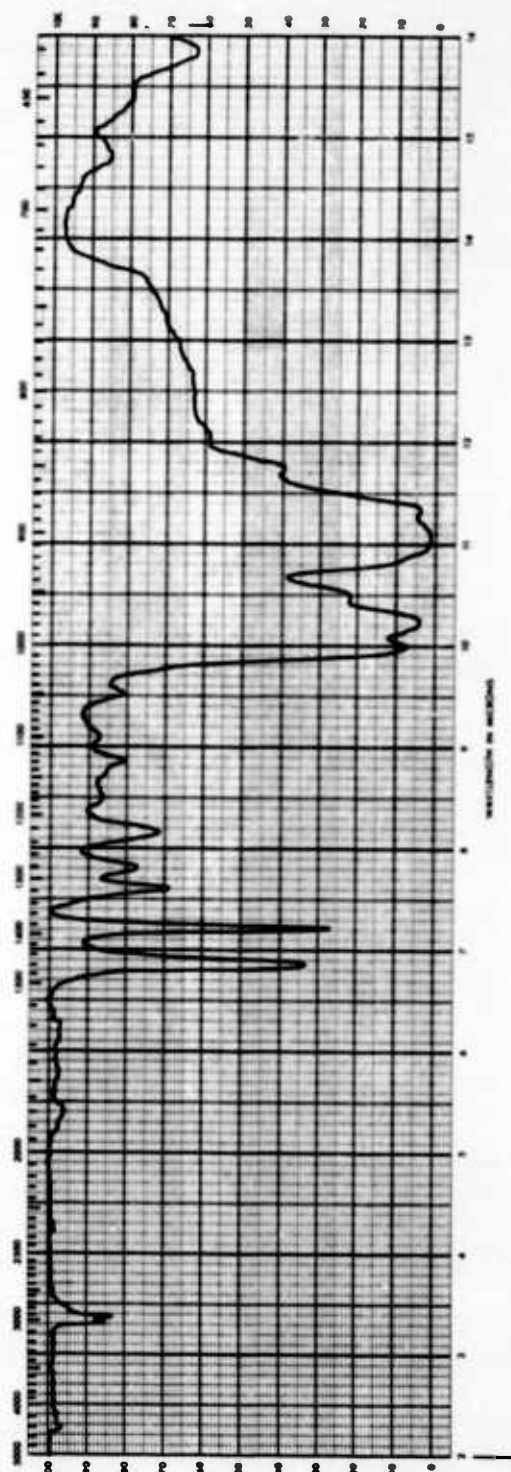
Fig. 2 Infrared Spectrum of 2,2,5,5-Tetrakis(difluoramino)hexane
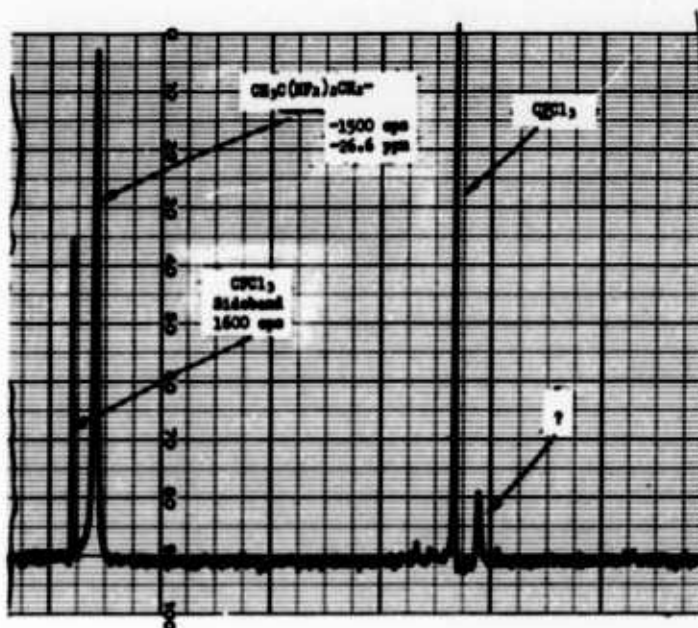
Fig. 3 F^{19} NMR Spectrum of 2,2,5,5-Tetrakis(difluoramino)hexane
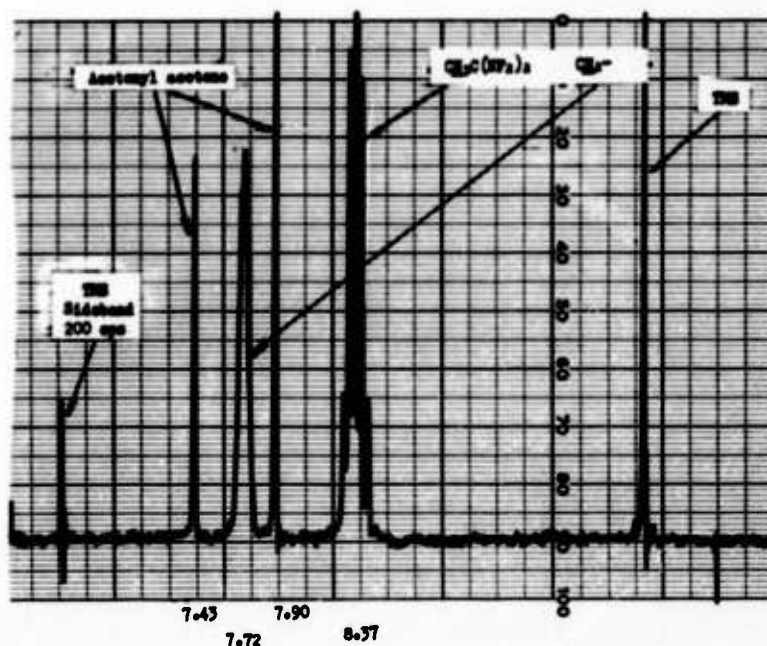
Fig. 4 Proton NMR Spectrum of 2,2,5,5-Tetrakis(difluoramino)hexane
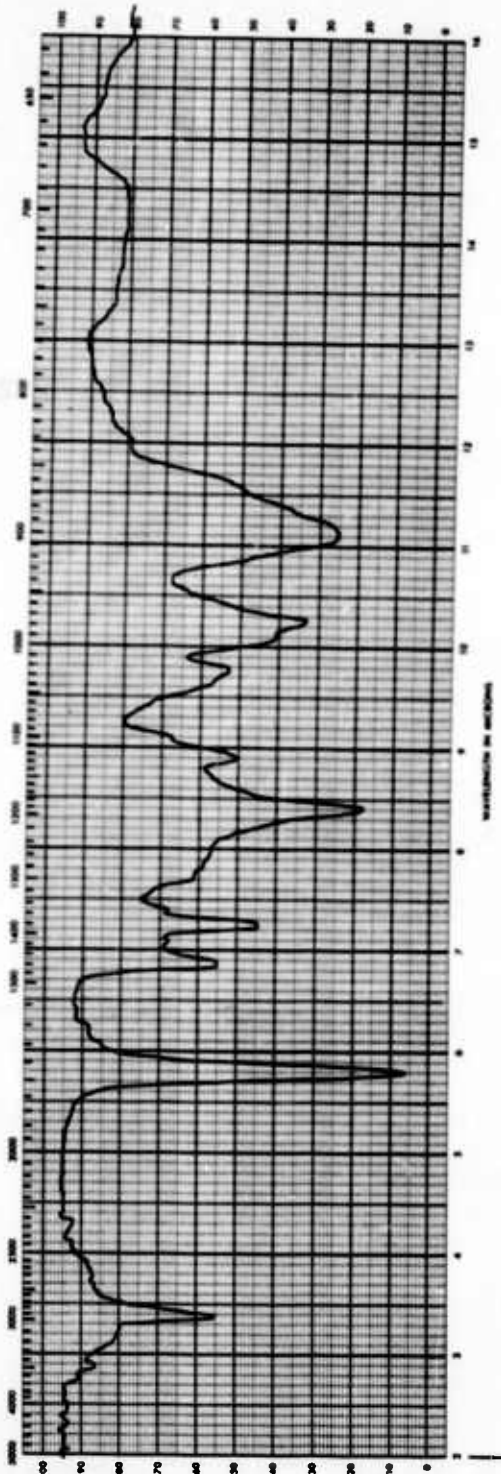
Fig. 5 Infrared Spectrum of Ethyl 5,5-bis(difluoraminohexanoate
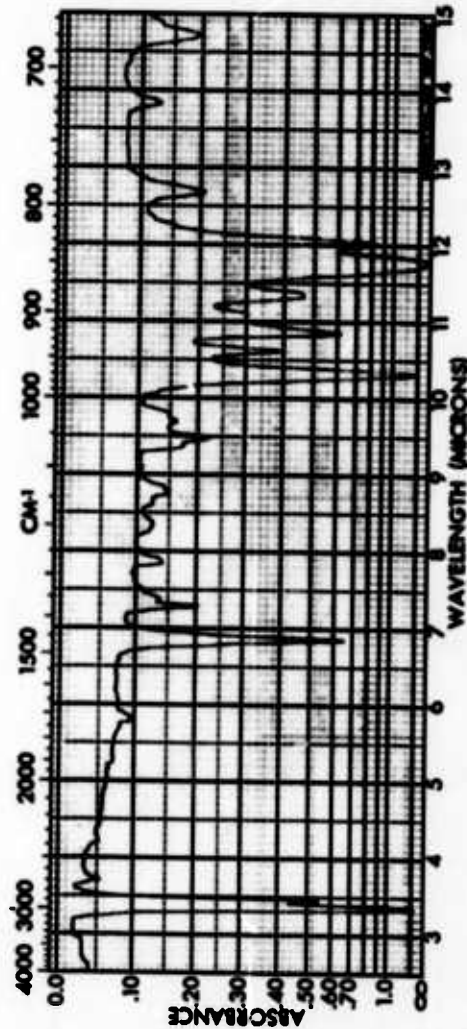
Fig. 6 Infrared Spectrum of Cyclohexyldifluoramine
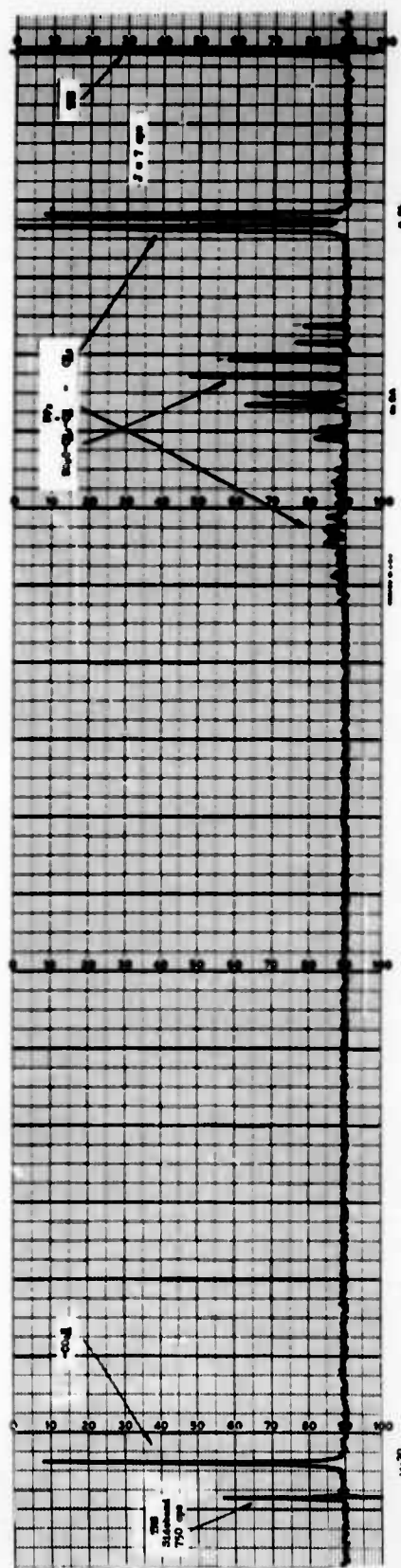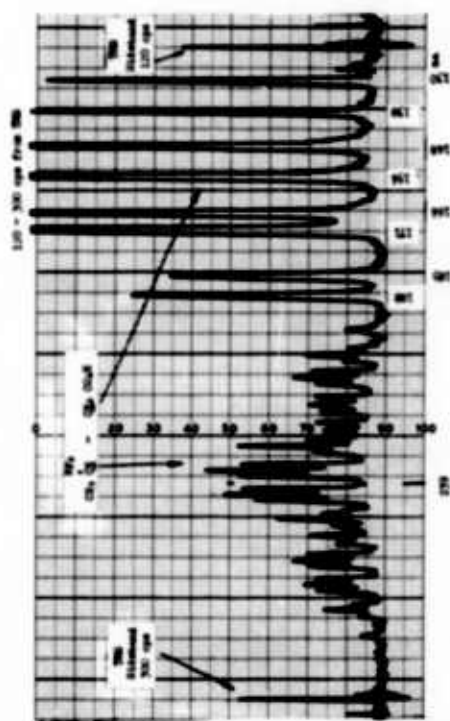
Fig. 7 Proton NMR Spectrum of Crotonic Acid Adduct
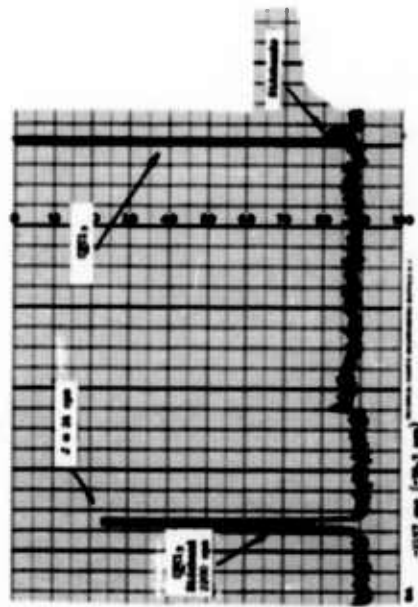
Figure 7

Fig. 8 F^{19} NMR Spectrum of Crotonic Acid Adduct
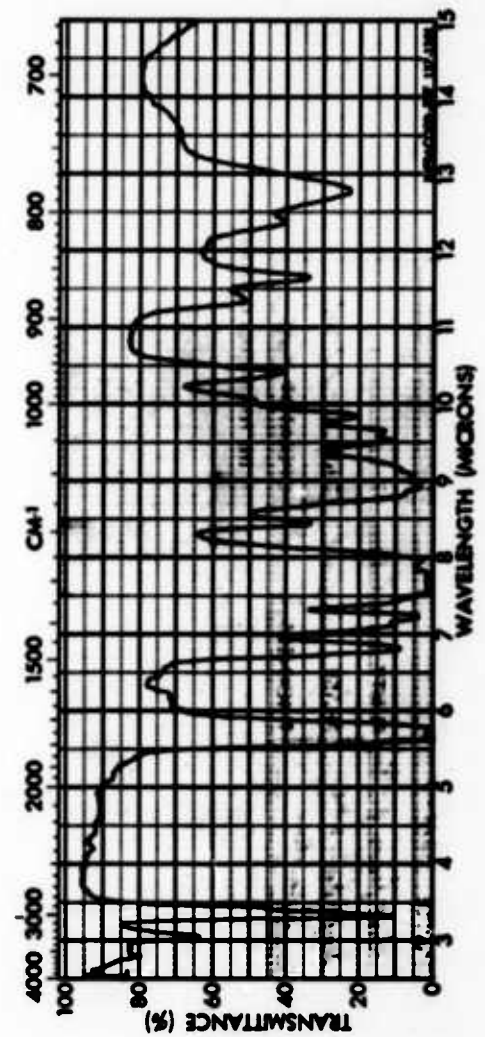
Fig. 9 Infrared Spectrum of Ethyl N-sec-butyl-N-fluorocarbamate
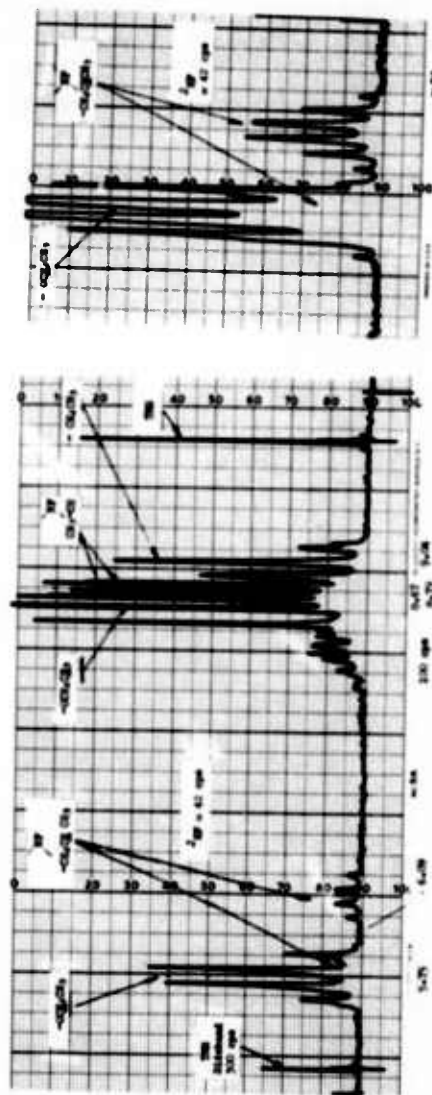
Fig. 10 Proton NMR Spectrum of Ethyl N-sec-butyl-N-fluorocarbamate
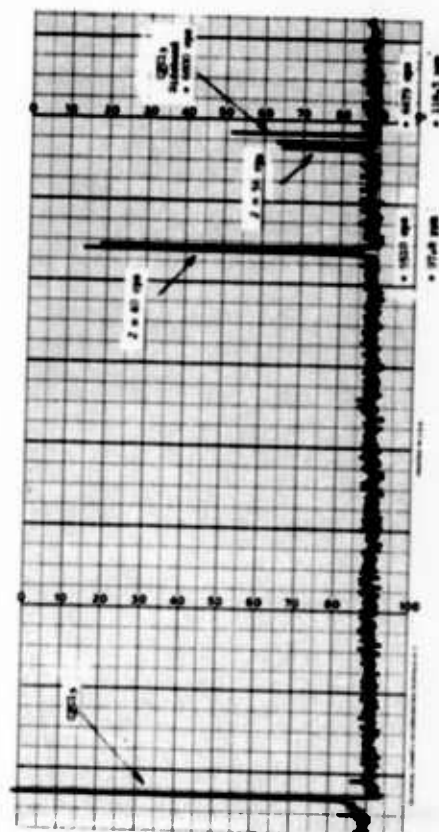
Fig. 11 F^{19} NMR Spectrum of Ethyl N-sec-butyl-N-fluorocarbamate
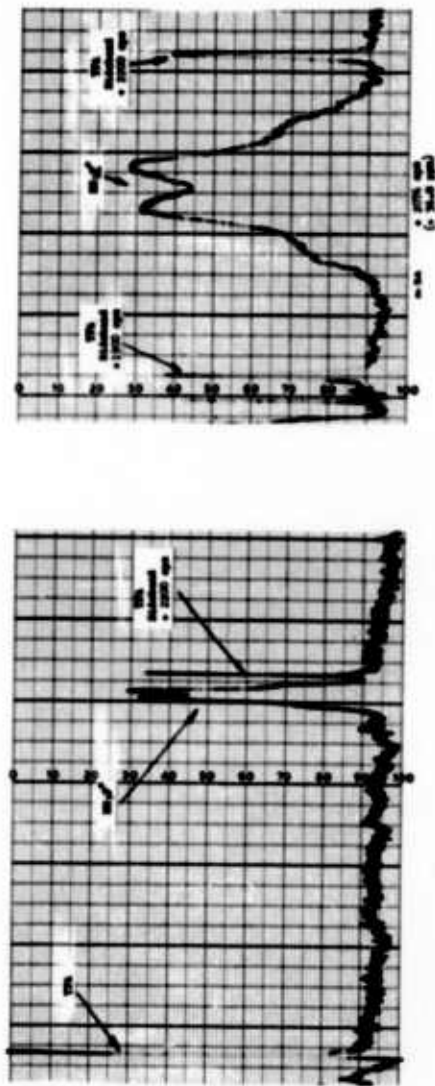
Fig. 12 F^{19} NMR Spectrum of N-Fluoroammonium Salt in Concentrated Sulfuric Acid
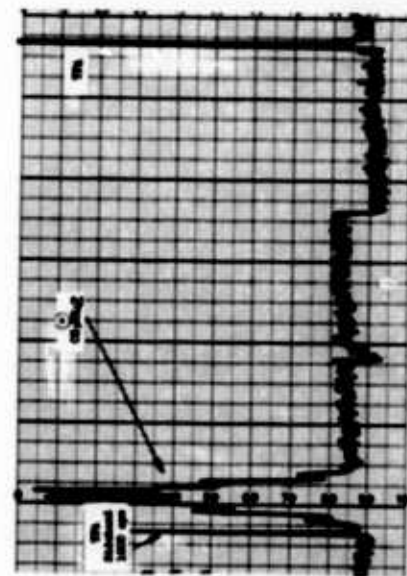
Fig. 13 F^{19} NMR Spectrum of N-Fluoromethylammonium Salt in Concentrated Sulfuric Acid
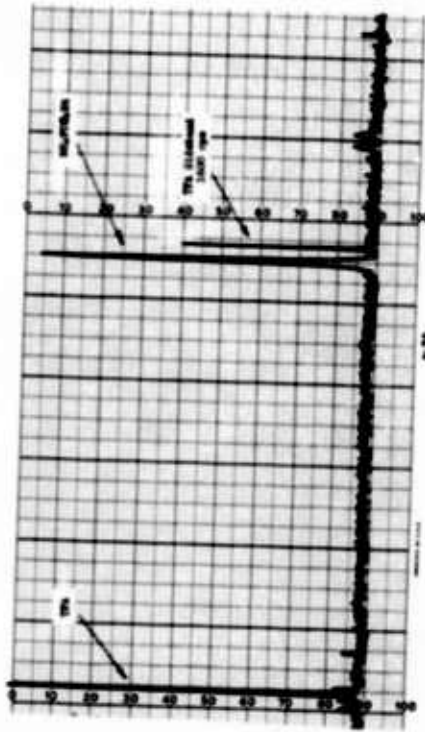
Fig. 14 F^{19} NMR Spectrum of Ethyl N-Fluorocarbamate in Concentrated Sulfuric Acid
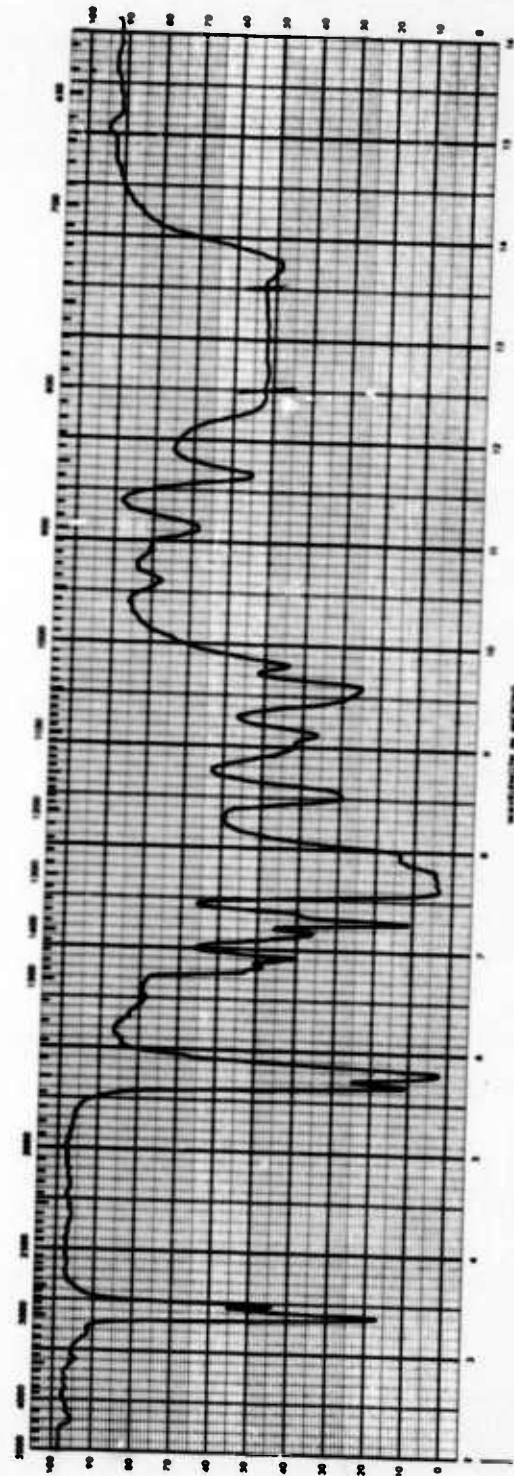
Fig. 15 Infrared Spectrum of Ethyl N-Cyclopenyl-N-fluorocarbamate
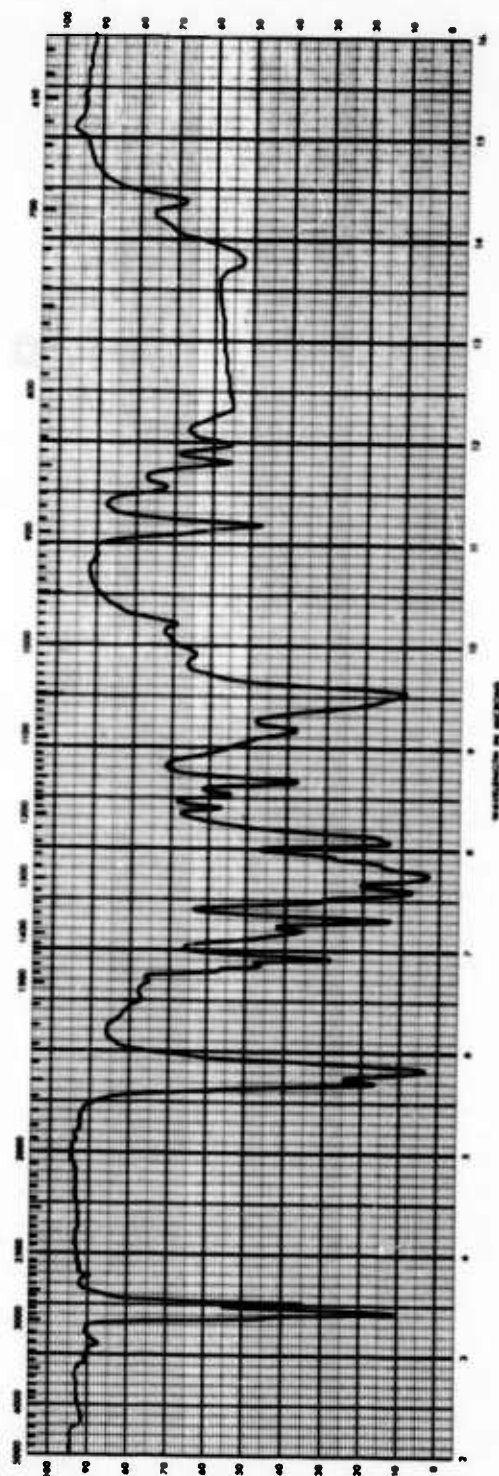
Fig. 16 Infrared Spectrum of Ethyl N-Cyclohexyl-N-fluorocarbamate
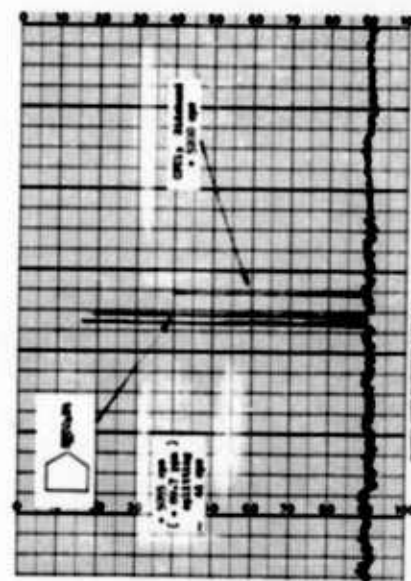
Fig. 17 F^{19} NMR Spectrum of Ethyl N-Cyclopentyl-N-fluorocarbamate
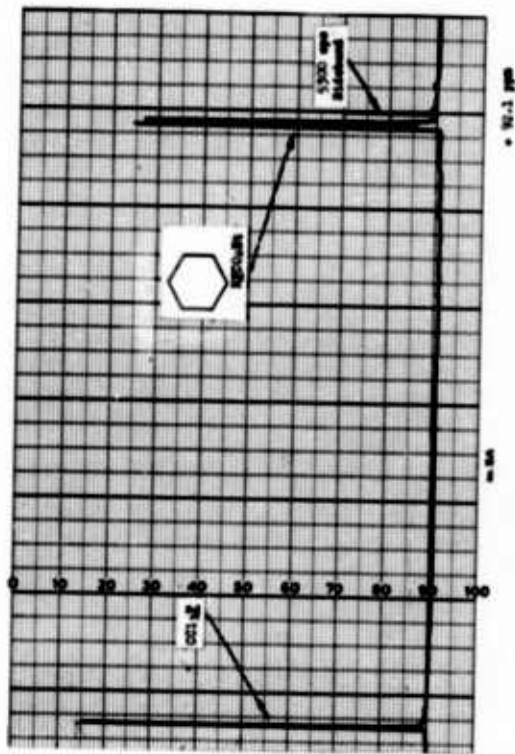
Fig. 18 F^{19} NMR Spectrum of Ethyl N-Cyclohexyl-N-fluorocarbamate
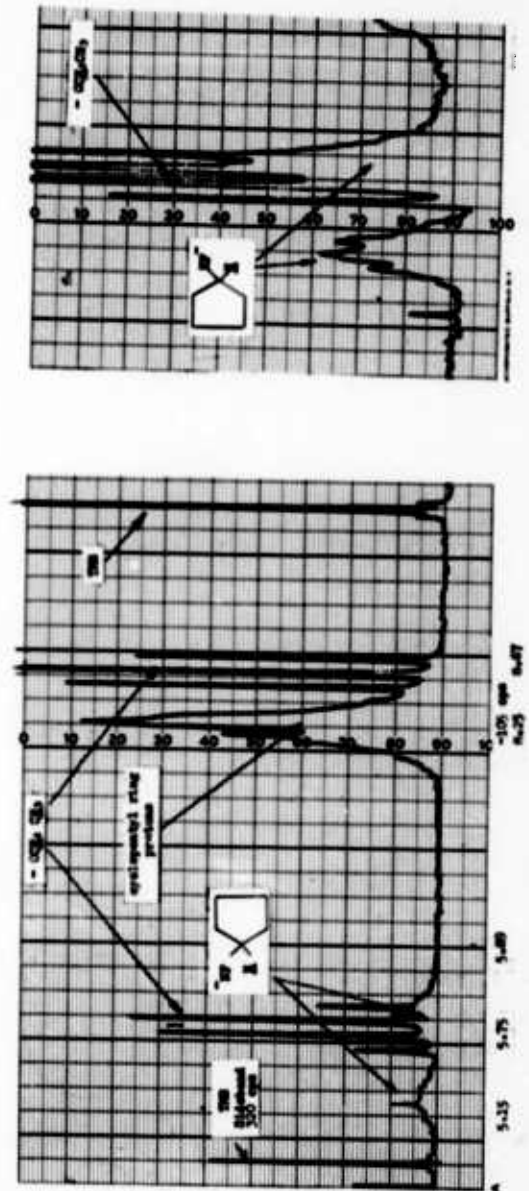
Fig. 19 Proton NMR Spectrum of Ethyl N-Cyclopentyl-N-fluorocarbamate
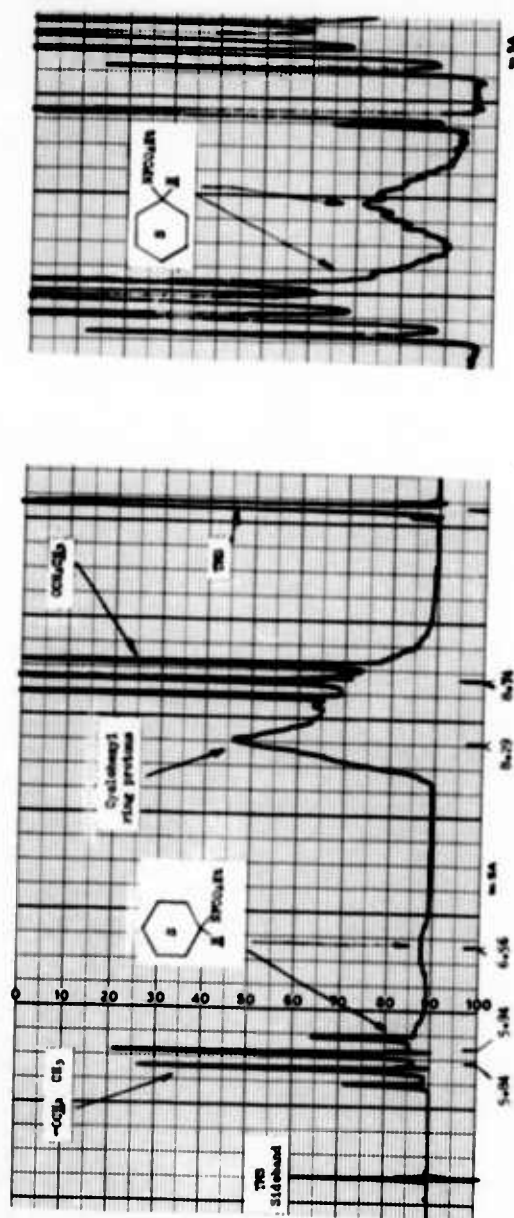
Fig. 20 Proton NMR Spectrum of Ethyl N-Cyclohexyl-N-fluorocarbamate
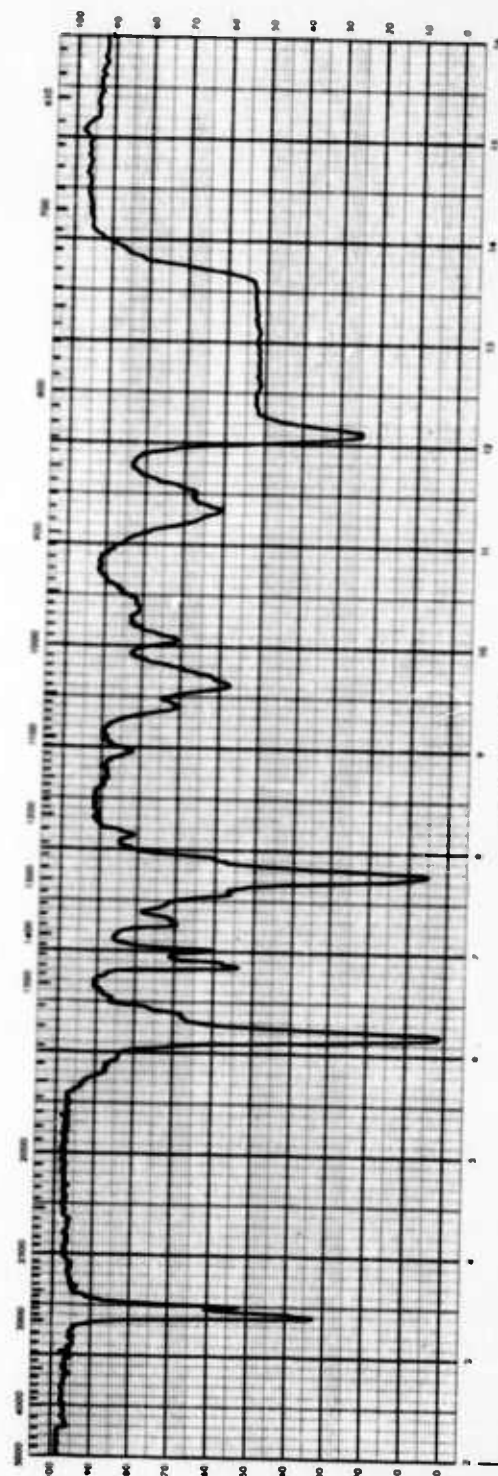
Fig. 21 Infrared Spectrum of N-Fluoro-N-nitro-n-butylamine
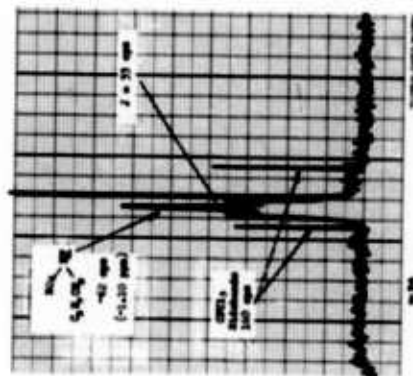
Fig. 22 F^{19} NMR Spectrum of N-Fluoro-N-nitro-n-butylamine
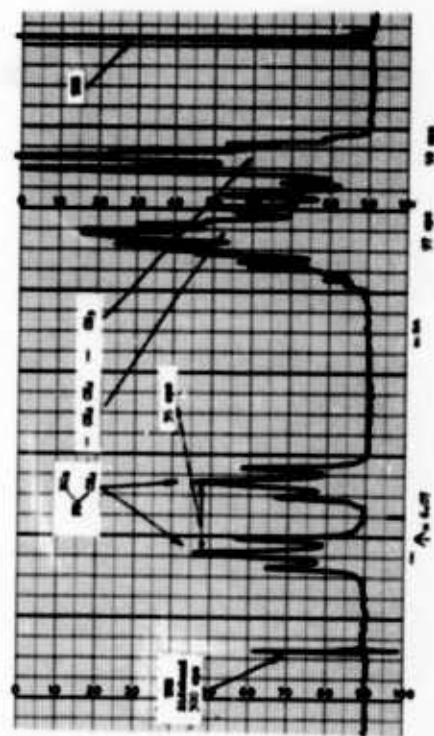
Fig. 23 Proton NMR Spectrum of N-Fluoro-N-nitro-n-butylamine

Figures 22 and 23
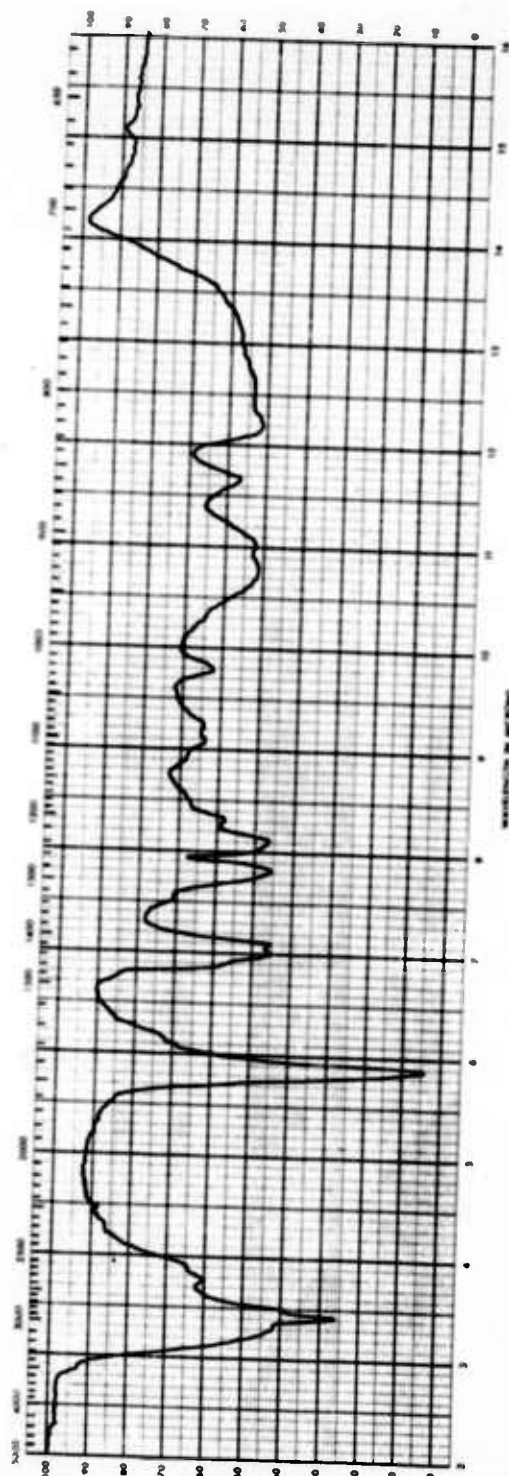
Fig. 24 Infrared Spectrum of 6-Difluoraminohexanoic Acid
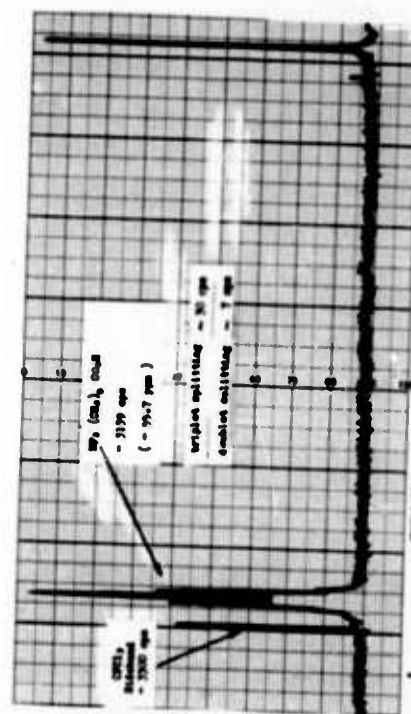
Fig. 25 F^{19} NMR Spectrum of 6-Difluoraminohexanoic Acid
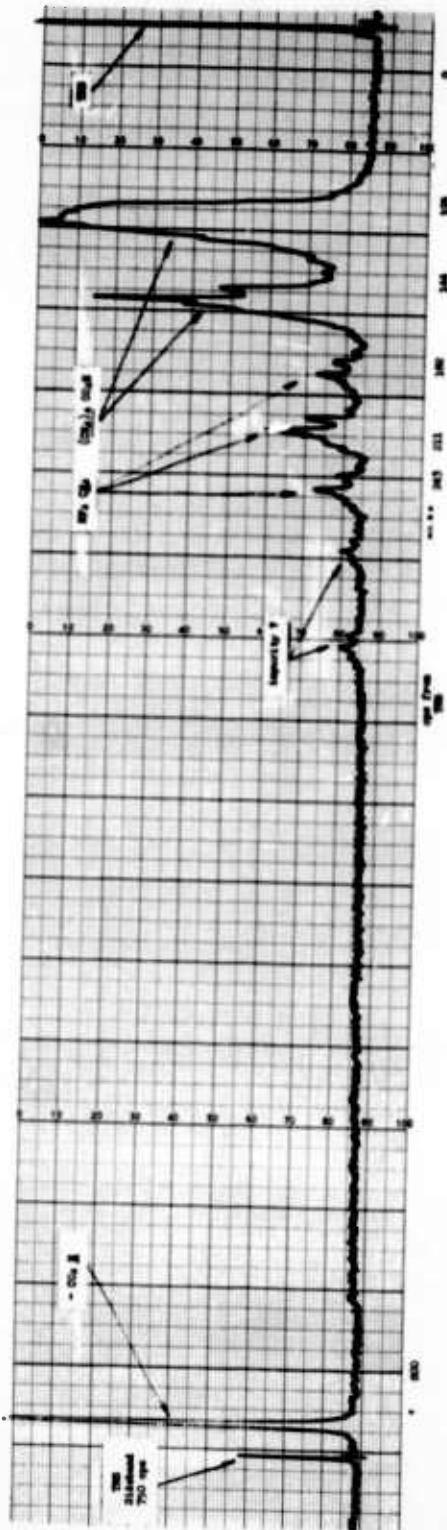
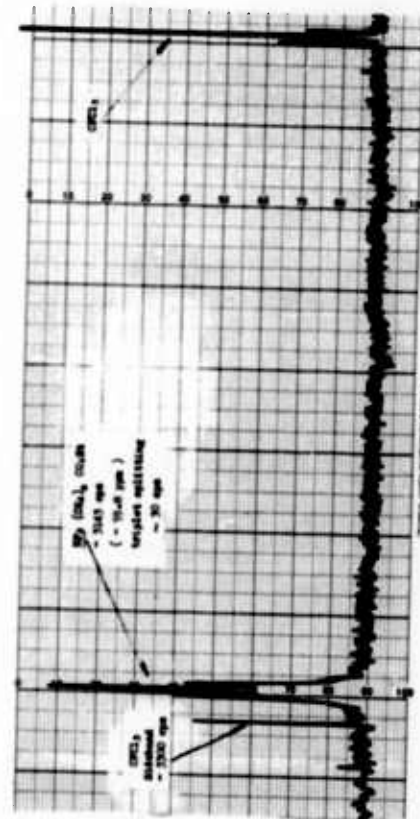Fig. 26   Proton NMR Spectrum of 6-Difluoraminohexanoic Acid

Fig. 27   F^{19} NMR Spectrum of Ethyl 6-Difluoraminohexanoate
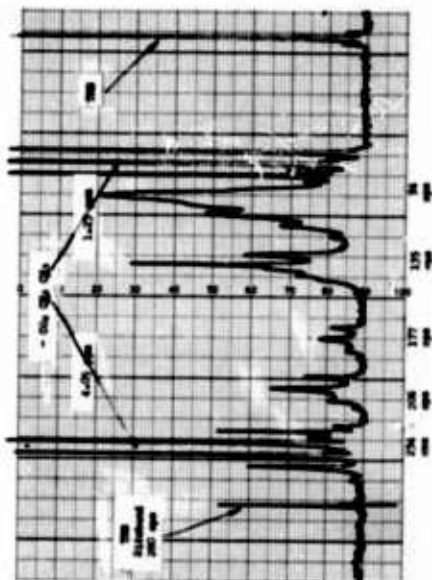
Fig. 28   Proton NMR Spectrum of Ethyl 6-Difluoraminohexanoate
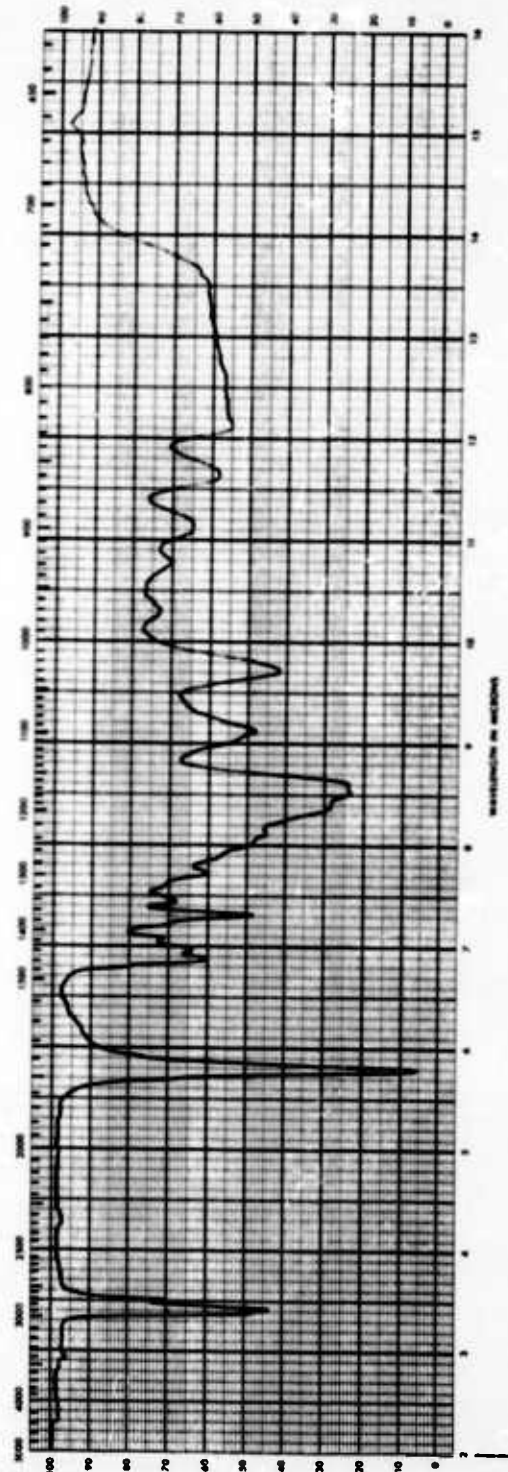

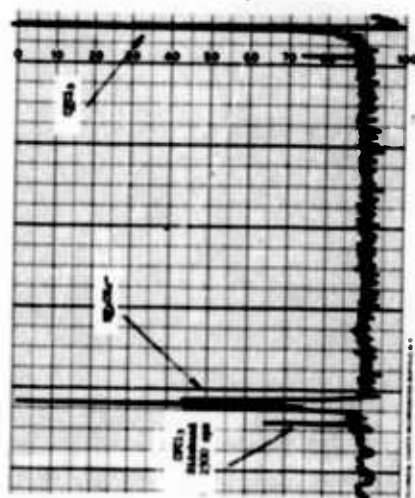Fig. 29   Infrared Spectrum of Ethyl 6-Difluoraminohexanoate

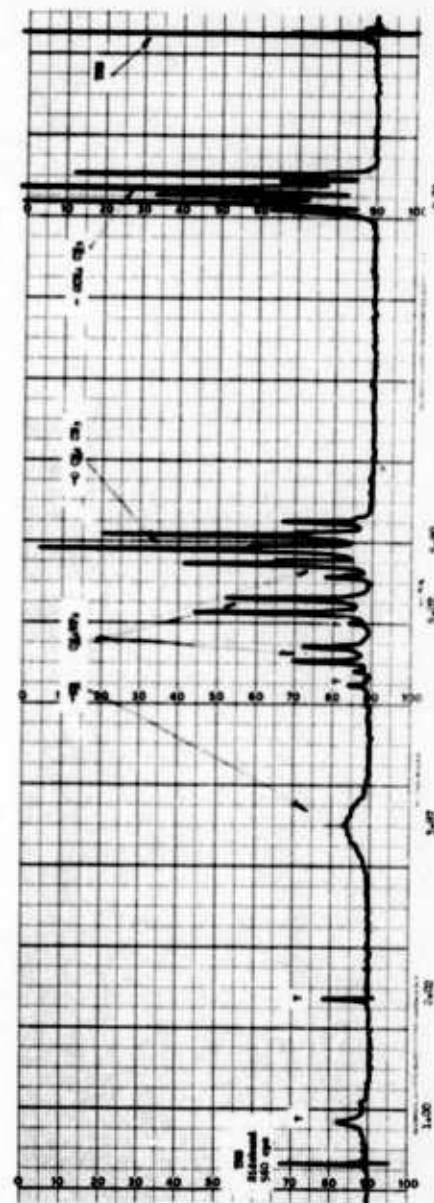Fig. 30   F^{19} NMR Spectrum of Ethyl N-Difluoraminomethylcarbamate

Fig. 31   Proton NMR Spectrum of Ethyl N-Difluoraminomethylcarbamate

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