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RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT TO

OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

MAY 1965

COPY NO. CP-61-16

CHEMICAL PRODUCTS DIVISION
AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

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CONFIDENTIAL

May 1965

Report No. 0235-01-22
(Quarterly)

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

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A Report to

OFFICE OF NAVAL RESEARCH
and
ADVANCED RESEARCH PROJECTS AGENCY

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Von Karman Center

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ABSTRACT

The reactions of 1-difluoraminobutane and 2-difluoraminobutane with concentrated sulfuric acid gave the ions, $CH_2{=}\overset{\oplus}{N}F\text{-}CH_2CH_2CH_3$ and $CH_3CH{=}\overset{\oplus}{N}FCH_2CH_3$, respectively. A 1:1 adduct of isoprene and difluoramine was obtained, using the boron trifluoride complex of phosphoric acid as catalyst. The reaction of 2,2-bis(difluoramino)octane with sulfuric acid, with vigorous agitation, gave 2-octanone. The reaction of α,α-dibromo-α-difluoraminotoluene with sodium 2-propanenitronate gave α-bromo-α-fluoriminotoluene.

The fluorination of ethyl methoxycarbamate gave N,N'-dimethoxy-N,N'-dicarbethoxyhydrazine instead of the expected NF derivatives.

Methyl α-difluoraminobutyrate was synthesized, and contrary to the reported difluoraminoacetate, the compound does not undergo dehydrofluorination on storage.

An NF-containing compound was obtained in the fluorination of 2,4,6-trichloroaniline. Instead of the originally expected 2,4,6-trichlorophenyldifluoramine, the compound appears to be a mixture of two fluoriminocyclohexadiene derivatives.

Synthesis, purification, and handling techniques in the preparation of fluoroammonium perchlorate were finalized and the compound now can be routinely prepared in lots of 2 to 3 grams.

Report No. 0235-01-22

CONTRACT FULFILLMENT STATEMENT

This is the twenty-second in a series of quarterly technical reports submitted in partial fulfillment of the contract. It covers the period 1 January through 31 March 1965.

AEROJET-GENERAL CORPORATION

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I. INTRODUCTION

The objective of this program is to develop new methods of preparing high-energy materials for military application. During the period covered in this report, research has continued on the reactions of difluoramine, on liquid phase fluorination of nitrogenous compounds, and the preparation of fluoroammonium perchlorate.

II. TECHNICAL DISCUSSION

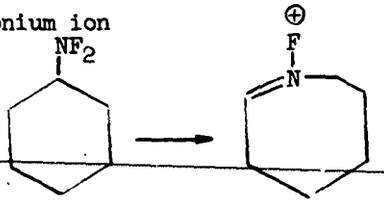
A. REACTIONS OF DIFLUORAMINE (K. Baum)

1. Discussion

The reactions of t-alkyldifluoramines with boron trifluoride or sulfuric acid have yielded N-fluoroimonium ions by the loss of fluoride, with concomitant alkyl migration.*

$$R_3CNF_2 \longrightarrow R_2\overset{\oplus}{C}=NF-R$$

The only primary and secondary alkyl difluoramines that were examined in this reaction (using sulfuric acid) were ethyldifluoramine and cyclohexyldifluoramine. The former compound underwent eliminations of HF to form acetonitrile rather than rearrangement to an imonium ion. The latter compound rearranged as expected to give the cyclic imonium ion



*Aerojet Report No. 2945, October 1964, p. 9 (Confidential).

The potential usefulness of this reaction for predicting side-products in difluoramine reactions prompted the investigation of addition primary and secondary derivatives. The syntheses of 1-difluoraminobutane and 2-difluoraminobutane by the fluorination of n-butylurea and N-(2-butyl)carbamate, respectively, were given in the preceding report.*

The reaction of 1-difluoraminobutane with sulfuric acid was expected to proceed in a way analogous to that of ethyldifluoramine, to give the nitrile

$$CH_3CH_2CH_2CH_2NF_2 \xrightarrow{?} CH_3CH_2CH_2CN$$

However, the NMR spectra of the solution formed by shaking 1-difluoraminobutane with sulfuric acid were consistent with the propyl migration product, N-fluoro-N-propyl-methyleneimonium ion

$$CH_3CH_2CH_2CH_2NF_2 \longrightarrow \begin{matrix} H & & F \\ & \diagdown\ \oplus\ \diagup & \\ & C = N & \\ H \diagup & & \diagdown CH_2CH_2CH_3 \end{matrix}$$

The proton NMR spectrum of the sulfuric acid solution is shown in Figure 1. The low-field group of signals is assignable to the "olefinic" protons. The inner two members are seen to be doublets, while the outer ones are broadened. It seems reasonable to assign the outer signals (8.41 ppm, j = 48 cps) to the proton trans to fluorine and the inner ones (8.38 ppm, j = 23 cps) to the cis proton. The splitting of the cis proton is attributed to geminal coupling to the trans proton. The trans proton signal would be broadened by allylic coupling to the α-methylene proton of the propyl group. The pair of triplets at 4.46 ppm is assignable to these α-methylene protons; the sextet at 2.10 ppm, to the next methylene, and the triplet at 1.12 ppm, to the methyl group.

*Aerojet Report No. 0235-01-21, February 1965, p. 7 (Confidential).

The F^{19} spectrum is given in Figure 2; an HF signal was observed at -116.55 ppm but is not shown in the figure. On the basis of the assignments of the "olefinic" protons, the NF signal would be expected to be a doublet (48 cps) of doublets (23 cps) of triplets (14 cps), as shown in the line spectrum. The predicted separation of the inner four members of the multiplet are 23, 25, and 23 cps; the observed separations are 21, 25, and 21 cps.

The reaction of 2-difluoraminobutane with sulfuric acid could be envisioned as taking place by any of three possible routes. Elimination of HF would give 2-fluoriminobutane, which would undergo a Beckmann rearrangement

$$CH_3CHNF_2CH_2CH_3 \xrightarrow{-HF} CH_3\overset{NF}{C}CH_2CH_3 \longrightarrow CH_3NHCOCH_2CH_3$$

or $CH_3CONHCH_2CH_3$

Methyl migration would give N-fluoro-N-methylpropylidenimonium ion:

$$CH_3CHNF_2CH_2CH_3 \longrightarrow CH_3\overset{\oplus}{N}F{=}CHCH_2CH_3$$

Ethyl migration, on the other hand, would give N-fluoro-N-ethylethylidenimonium ion:

$$CH_3CHNF_2CH_2CH_3 \longrightarrow CH_3CH_2\overset{\oplus}{N}F{=}CHCH_3$$

When 2-difluoraminobutane was shaken with concentrated sulfuric acid at 0°C, a homogeneous solution was formed. The proton and fluorine NMR spectra of this solution showed that the latter course was followed. Thus, the F^{19} spectrum (Figure 3) consists of an overlapping pair of triplets at -122.67 ppm and a singlet at -116.79, assignable to HF. The proton spectrum (Figure 4) contains a pair of quartets at 4.44 ppm and a triplet at 1.65 ppm which are attributable to the ethyl group. A pair of quartets at 8.54 ppm is in agreement with the signal expected for the "olefinic" proton of the ethylidene group. The methyl signal appears as a pair of doublets at 2.67 and 2.61 ppm.

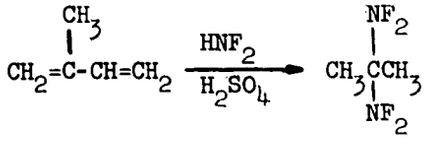
Peaks marked with an asterik are not assignable on the basis of the proposed structure, and are due to side-products or decomposition products.

Acetaldehyde, the expected hydrolysis product, was found to be unstable under the reaction conditions, condensing to give crotonaldehyde in a very short time. Crotonaldehyde showed peaks at 2.50 and 2.63 ppm. Recording only the 2.5- to 3.1-ppm portion of the spectrum immediately after a fresh sample was prepared gave the curve showing the absence of these impurities (Figure 5).

The presence of two doublets for this methyl group is indicative of the presence of cis and trans formed (i.e., rotation about the imonium double bond is slower than is observable by NMR at this coupling constant). On the other hand, the absence of separate signals for the cis and trans configurations of the "vinyl" hydrogen and the observed 37-cps HF coupling constant, close to the average of the cis and trans signals for the 1-difluoraminobutane product, indicate averaging. The expected chemical shifts of the cis and trans protons should differ by about 0.03 ppm, by analogy to the observed shifts of the 1-difluoraminobutane product. Apparently the rate of rotation about the C-N bond is such as to average the smaller difference but not the larger one.

These results indicate a much higher migratory aptitude for higher alkyl groups than for methyl groups in this reaction. For the 2-difluoraminobutane product, a minor portion of the proton spectrum consists of peaks not assignable to the ethyl migration product. The fluorine spectrum does not indicate other products, although the resolution is limited. The reaction of 1-difluoraminobutane with sulfuric acid consisted almost entirely of rearrangement with propyl migration, although ethyldifluoramine underwent only elimination.

The reaction of isoprene with difluoramine in sulfuric acid has yielded 2,2-bis(difluoramino)propane.*



This reaction, of possible utility for preparing high-energy propellant ingredients, may involve an alkyldifluoramine rearrangement similar to those above. The

*Aerojet Report No. 2099, November 1961, p. 11 (Confidential).

reaction was therefore repeated under conditions which do not normally result in rearrangement, using $BF_3 \cdot H_3PO_4$ as the catalyst. The product was a 1:1 adduct, as shown by elemental analysis, but NMR analysis to determine the direction of addition has not yet been performed. The reaction of the adduct with sulfuric acid will be studied.

Although gem-difluoramines are stable in sulfuric acid under the preparative conditions, the possibility of reaction with sulfuric acid in the absence of difluoramine was examined. When a mixture of 2,2-bis(difluoramino)-octane and concentrated sulfuric acid was agitated vigorously at room temperature for 1 hour, a homogeneous solution was formed. The F^{19} NMR spectrum of this solution showed that HF was the only fluorine species present. The solution was quenched with ice and extracted with methylene chloride. The infrared spectrum of the methylene chloride solution showed only 2-octanone. The reaction of ketones with difluoramine is thus readily reversible.

The reactions of α,α-dibromo-α-difluoraminotoluene, α-bromo-α,α-bis(difluoramino)toluene and α-difluoramino-α,α-dichlorotoluene with sodium methoxide gave dimethyl carbonate anil.* Some reactions of these NF compounds with other basic reagents were also explored. Reactions with tertiary amines gave only tars. Secondary amines gave products which appeared, on the basis of infrared spectra, to be the tetraalkylguanidines corresponding to the above reactions, but elemental analyses were unsatisfactory.

The sodium 2-propanenitronate in methanol reacted with α,α-dibromo-α-difluoraminotoluene to give α-bromo-α-fluoriminotoluene. Although an uncontaminated sample could not be obtained by gas chromatography; elemental analysis was in fair agreement with the theoretical values; and the structure was confirmed by infrared (Figure 6), proton (Figure 7), and fluorine (Figure 8) NMR spectra.

$$C_6H_5CBr_2NF_2 \xrightarrow{(CH_3)_2CNO_2^{\ominus}} C_6H_5\underset{\underset{Br}{|}}{C}=NF$$

*Aerojet Report No. 0235-01-21, February 1965, p. 3 (Confidential).

A reduction of this type is probably the first step in the methoxide reaction leading to dimethyl carbonate anil. In the nitronate reaction, subsequent addition to the fluorimino could be inhibited because of the size of the anion.

2. Experimental

a. Reaction of Alkyldifluoramines with Sulfuric Acid

The alkyldifluoramine (0.05 ml) was added to 1 ml of sulfuric acid at 0°C in a stoppered test tube. The tube was agitated with a vortex mixer, with intermittant cooling with an ice bath, until a homogeneous solution was formed. NMR spectra of these solutions were obtained.

b. Reaction of Isoprene with Difluoramine

Boron trifluoride complex of phosphoric acid (1 ml) was added with stirring to a refluxing mixture of 5 g of isoprene and 27 g of difluoramine. After 2.5 hours, 50 ml of pentane was added and the excess difluoramine was vented off. Distillation of the pentane solutions gave 0.35 g of liquid, bp 52°C/0.15 mm.

Anal. Calc'd for $C_5H_9NF_2$: C, 49.5; H, 7.34; N, 11.55; F, 31.40.

Found: C, 48.5; H, 7.12; N, 12.1; F, 29.9.

c. Reaction of Dibromodifluoraminotoluene with Sodium 2-Propane-Nitronate

A solution of sodium 2-propanenitronate was prepared by refluxing a mixture of 11.1 ml (0.0163 moles) of 1.47 M methanolic sodium methoxide and 1.45 g (0.0163 moles) of 2-nitropropane for 30 min. This solution was cooled to room temperature and 2.45 g (0.00815 moles) of dibromodifluoraminotoluene in 35 ml of methanol was added over a 15 min period. After 1 hour, the methanol was removed under vacuum and hexane was added. The hexane solution was filtered and distilled to give 0.98 g of liquid, bp 52°C/0.75 mm.

Gas chromatography (1/4-in. by 12 ft column of 10% SE-30 silicone on Teflon, 110°C) showed a major component comprising 85% of the sample

and six volatile contaminants. Characterization of the major component indicated that it was α-bromo-α-fluoriminotoluene, with some impurities.

Anal. Calc'd for C_7H_5NFBr: C, 41.6; H, 2.48; N, 6.94; F, 9.4.

Found: C, 42.0; H, 2.64; N, 8.47; F, 10.1.

The infrared spectrum is shown in Figure 6. The proton and fluorine NMR spectra (Figures 7 and 8, respectively) were obtained using a Varian microcell, with $CDCl_3$ as solvent and $CFCl_3$ and TMS as internal references. The proton spectrum consists of a complex aromatic multiplet with prominent absorptions at 448 and 463 cps, a doublet at 4.09 ppm, and a singlet at 1.68 ppm (caused by impurities). The fluorine spectrum consists of a somewhat broadened fluorimino band at -64.1 ppm.

B. DIRECT FLUORINATION (V. Grakauskas)

1. Discussion

The study of liquid-phase fluorination of nitrogenous organic compounds was continued using acetonitrile as the solvent.

The fluorination of ethyl methoxycarbamate in acetonitrile was investigated with the objective of synthesizing either its N-fluoro derivative or O-methyl-N,N-difluorohydroxylamine:

$$CH_3ONHCO_2C_2H_5 + F_2 \not\longrightarrow CH_3ONFCO_2C_2H_5 \xrightarrow{F_2} CH_3ONF_2$$

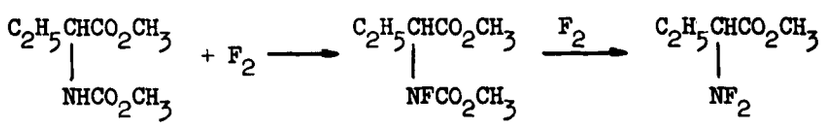
Neither compound was obtained; instead the reaction product was identified as N,N'-dimethoxy-N,N'-dicarbethoxyhydrazine on the basis of its elemental analysis, and its infrared (Figure 9) and proton NMR Spectra. The compound apparently was formed in a coupling reaction between N-fluoro-N-methoxycarbamate and methoxycarbamate:

$$CH_3ONFCO_2C_2H_5 + CH_3ONHCO_2C_2H_5 \xrightarrow{-HF} \begin{matrix} CH_3ONCO_2C_2H_5 \\ | \\ CH_3ONCO_2C_2H_5 \end{matrix}$$

N,N'-Dimethoxy-N,N'-dicarbethoxyhydrazine represents the first known N-alkoxy-substituted hydrazine derivative. One unsuccessful attempt was made to hydrolyze the compound to N,N'-dimethoxyhydrazine; it reacted readily with cold concentrated hydrochloric acid with the evolution of carbon dioxide, but only a trace amount of an unidentified solid was isolated from the reaction mixture.

N,N'-Dimethoxy-N,N'-dicarbethoxyhydrazine appears to be an interesting substrate for studying its fluorination and in order to obtain larger amounts of the compound one attempt was made to "couple" ethyl methoxycarbamate with bromine in carbon tetrachloride solution; however, reaction did not take place at ambient temperature.

Ethyl difluoraminoacetate was previously obtained in the fluorination of ethyl N-carbomethoxyglycine.* The compound, however, could not be separated completely from its dehydrofluorination product, ethyl cyanoformate. It appeared that the instability of α-difluoraminocarboxylic acid esters might be characteristic only to the first member of the series, and now has been found to be the case. Methyl α-difluoraminobutyrate, synthesized in the fluorination of methyl α-carbomethoxyaminobutyrate in acetonitrile solution, was found to be stable and storable at room temperature.



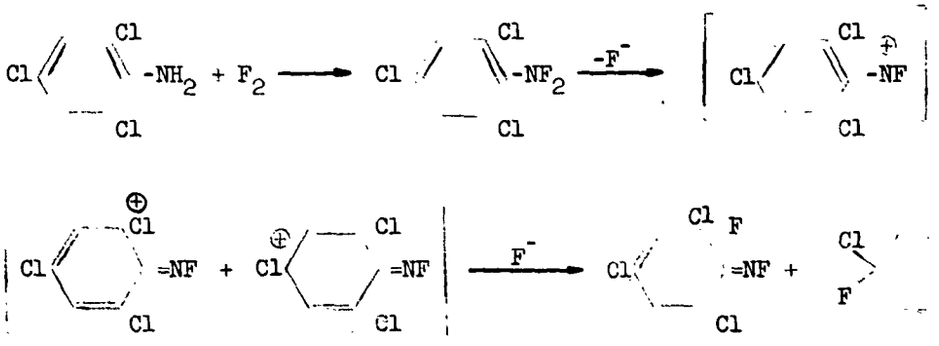
The compound was characterized on the basis of its elemental analysis, and its infrared (Figure 10) and NMR (Figures 11 and 12) spectra.

Methyl α-(N-carbomethoxy-N-fluoro)aminobutyrate was also obtained in the above fluorination and the compound was fully characterized by its infrared and NMR spectra (Figures 13, 14, and 15).

The fluorination of aromatic nitrogenous compounds was attempted on several occasions in the past, but the reaction produced large amounts of tar

*Aerojet Report No. 2730 (Annual Summary), October 1963, p. 25 (Confidential).

and isolation and characterization of reaction products was found impossible. From these unsuccessful attempts, it was learned that the fluorination of negatively substituted aromatic compounds proceeds "cleaner." However, the solubility of such substrates in water is extremely low and the fluorination under such conditions is impractical. The finding that acetonitrile is a very suitable solvent for liquid phase fluorination, in conjunction with the increased solubility of organic compounds in this solvent, suggested that the fluorination of aromatic nitrogenous compounds might proceed better under these conditions than in aqueous suspensions. On the basis of these considerations, the fluorination of 2,4,6-trichloroanaline was investigated. The fluorination still was sluggish and the reaction mixture turned gradually black during the course of the reaction. However, on working up the product by fractional distillation, a small amount (ca. 5% yield) of liquid was obtained and its elemental analysis compared well with that calculated for 2,4,6-trichlorophenyldifluoramine. Its proton NMR spectrum (Figure 16), however, indicated that the compound was not the desired difluoramino derivative, but most likely a mixture of two trichlorocyclohexadienefluorimino isomers. The reaction can be rationalized by the formation of the difluoramine, followed by its rearrangement:



The infrared spectrum of the material is shown in Figure 17. The rearrangement might have taken place spontaneously during the process of fluorination. On the other hand, it is also possible that it was effected during the fractionation of the crude reaction product when the mixture was kept at 70 to 90°C for a period of several hours.

2. Experimental

a. Fluorination of Ethyl Methoxycarbamate

A solution of 18 g (0.15 mole) of ethyl N-methoxycarbamate in 120 ml of acetonitrile was fluorinated at -15 to -25°C until 3.5 liters of fluorine (~0.15 mole) was consumed. The fluorination mixture was added to 550 ml of ice water and insoluble material was separated and worked up to give 3 g of a pale-yellow oil, bp 90 to 91°C/0.1 mm, which was identified as N,N'-dimethoxy-N,N'-dicarbethoxyhydrazine.

Anal. Calc'd for $C_8H_{16}N_2O_6$: C, 40.68; H, 6.83; N, 11.86.

Found: C, 40.3; H, 6.4; N, 11.9.

DTA of this compound showed a strong exotherm at 142°C. Its infrared spectrum is shown in Figure 9. The 60-mc proton NMR spectrum was obtained, using a $CDCl_3$ solution with TMS added as an internal reference. The assignments are as follows: the triplet at 1.33 ppm and the quartet at 4.31 ppm are assigned to the ethyl group; the intense singlet at 3.87 ppm is assigned to the methoxy methyl group.

b. Fluorination of Methyl α-Carbomethoxyaminobutyrate

Methyl α-carbomethoxyaminobutyrate was synthesized by reacting DL-α-aminobutyric acid with methyl chloroformate in aqueous sodium hydroxide solution to give α-carbomethoxyaminobutyric acid which was then esterified with methanol. The material, bp 75 to 6°C/0.1 mm, was obtained in 85% yield.

Anal. Calc'd for $C_7H_{13}NO_9$: C, 48.0; H, 7.5; N, 8.0.

Found: C, 47.8; H, 7.8; N, 8.4.

A solution of 70 g (0.4 mole) of methyl α-carbomethoxyaminobutyrate in 300 ml of acetonitrile was fluorinated at 0 to 5°C until ca. 0.7 moles of fluorine was consumed. The fluorination mixture was washed with 600 ml of ice water, phases separated, and the product was washed with three 150-ml portions of ice water. The crude material, 65 g, was dried and worked up to give

22 g of methyl α-difluoraminobutyrate, bp 52 to 3°C/40 mm, and 34 g of methyl α-(N-carbomethoxy-N-fluoramino)butyrate, bp 48 to 9°C/0.3 mm.

The infrared spectrum of methyl α-difluoraminobutyrate is shown in Figure 10.

Anal. Calc'd for $C_5H_9NF_2O_2$: C, 39.2; H, 5.92; N, 9.15; F, 24.81.

Found: C, 39.5; H, 6.1; N, 9.5; F, 23.4.

The 60-mc proton (Figure 11) and 56.4-mc fluorine (Figure 12) NMR spectra were obtained using $CDCl_3$ solution with TMS and $CFCl_3$ added as internal references. The assignments are as follows:

H'. The triplet at 1.03 ppm is assigned to the $C\underline{H}_3CH_2$- methyl group. The slightly irregular quartet at 1.95 ppm is assigned to the $CH_3C\underline{H}_2CH$- methylene. The asymmetry of the carbon to which it is attached appears to have little effect on the signal. The intense singlet at 3.81 ppm is assigned to the carbomethoxy methyl group. The doublet of doublets (coupling constants of 25.7 ±0.7 cps and 24.4 ±0.8 cps, coupling to nonequivalent NF_2 fluorines) of triplets (coupling to adjacent $-CH_2-$) at 4.10 ppm is assigned to the $-CH_2C\underline{H}NF_2-$ proton.

F^{19}. The fluorine spectrum consists of an AB quartet (chemical shifts -43.10 and -50.66 ppm, coupling constant 592.4 ±0.4 cps). The fluorines are rendered nonequivalent by the virtue of the attachment of the $-NF_2$ group to an asymmetric carbon. The quartet components are further split into doublets (25.5 ±0.8 cps, 24.0 ±0.8 cps) by coupling to the proton on that carbon. The observed coupling constants are in good agreement with those obtained from the proton spectrum. The proton and fluorine NMR spectra are consistent with each other and with the methyl α-difluoraminobutyrate structure.

The infrared spectrum of methyl α-(N-fluoro-N-carbomethoxy)aminobutyrate is shown in Figure 13.

Anal. Calc'd for $C_7H_{12}NFO_4$: C, 43.5; H, 6.3; N, 7.3; F, 9.8.

Found: C, 43.5; H, 6.2; N, 7.4; F, 10.5.

The 60-mc proton (Figure 14) and 56.4-mc fluorine (Figure 15) NMR spectra were obtained in $CDCl_3$ solution, with TMS and $ClCl_3$ added as internal references. The assignments are as follows:

H'. The triplet at 1.10 ppm is assigned to the CH_3CH_2- methyl group. The multiplet with the maximum intensity at 124 cps is assigned to the CH_3CH_2CH- methylene. The complex nature of this signal is attributable to the asymmetry of the carbon to which the methylene is attached and probably also to a small coupling to the -NF- fluorine. The intense singlets at 3.79 and 3.92 ppm are assigned to the carbomethoxy methyls. Each appears to be accompanied by a weaker signal to high field. This may be a consequence of partial double bond character of the -N-C- bond with resultant cis-trans isomerism. The doublet (40.5 ±0.6 cps, coupling to NF fluorine) of doublets of doublets (different couplings to the $-CH_2$- protons) at 4.59 ppm is assigned to the $-CH_2CHNF$- proton.

F^{19}. The fluorine spectrum consists of a strong doublet (40.8 ±0.5 cps) at +81.43 ppm and a weaker doublet (11.2 ±0.5 cps) at +79.98 ppm. The splitting in the stronger doublet is in excellent agreement with that observed in the proton spectrum and the signal is assignable to the -NFCO- fluorine. The weaker doublet may then be assigned to the corresponding cis or trans isomer. In this case, however, the large difference in the splittings is difficult to explain.

c. Fluorination of 2,4,6-Trichloroaniline

A solution of 19.6 g (0.1 mole) of 2,4,6-trichloroaniline in 200 ml of acetonitrile was fluorinated at 0°C until 4.5 liters of fluorine was

consumed. The fluorination mixture was added to 700 ml of ice water and phases were separated. The dark, viscous organic product was washed with water and dissolved in 75 ml of methylene chloride. The dried solution was worked up to give 2.0 g of orange-yellow liquid, bp 45 to 50°C/0.2 mm. The elemental analysis of the product was in excellent agreement with that calculated for 2,4,6-trichlorophenyldifluoramine.

Anal. Calc'd for $C_6H_2NF_2Cl_3$: C, 31.0; H, 0.9; N, 6.0; F, 16.4.

Found: C, 31.2; H, 1.1; N, 5.2; F, 16.4.

The infrared spectrum of the material is shown in Figure 17.

The 60-mc proton NMR spectrum (Figure 16) was obtained using $CDCl_3$ solution, with TMS added as internal reference. The spectrum is quite complex, consisting of a multiplet (or group of multiplets) at low field, with prominent lines at 394, 409, 430, and 436 cps and a much weaker group of signals to high field (most intense line at 137 cps). Other weak, broad signals are also apparent. The low-field signals are in the region usually characteristic of aromatic protons. However, olefinic protons also may appear in this vicinity.

The spectrum is much too complicated for the symmetrical difluoro-2,4,6-trichloroaniline. However, if the rotation of the difluoramino group is hindered by the ortho chlorines, the NF_2 fluorines would be rendered non-equivalent which might complicate the proton spectrum considerably. The complexity could also result from the presence of a mixture of the two rearrangement products.

The fluorine NMR spectrum has been obtained only in a preliminary manner using $CFCl_3$ as internal reference. The spectrum appears to consist of two groups of signals, one in the vicinity of -30 ppm and the other near +100 ppm. This information rules out the presence of the difluoramino derivatives alone, since it offers no explanation of the signals to the high field. These signals are in the region characteristic of CF fluorines, suggesting the presence of either one or both rearrangement products. The low-field signals are attributable to =NF or $-NF_2$ fluorines or a combination of both.

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

1. Discussion

During this report period, several 2-3 g batches of N-fluorammonium perchlorate (SAP) were prepared for physical and chemical testing. The material was routinely purified by sublimation at 65°C/0.05 mm. Although sublimation sufficed as a purification technique for the 2- to 3-g quantities, anticipation of the need for larger amounts of SAP prompted the investigation of an alternate purification method. It was found the crude SAP could be purified by liquid-solid chromatography on silica gel using ethyl acetate as the eluent, followed by precipitation with chloroform. Elemental analysis and proton NMR spectrum showed that SAP purified in this manner did not contain foreign materials.

The infrared spectrum of SAP is given in Figure 18. The spectrum was obtained by subliming SAP onto a sodium chloride window. The N-F absorption is apparently obscured by the $-ClO_3$ absorption; both NH-stretch (3.05μ) and NH-bend (7.03μ) vibrations are shifted by approximately 0.15μ to shorter wavelength as compared with those of ammonium perchlorate.

The X-ray powder diffraction pattern is given in Table 1 .

Some additional solubility data for SAP is given in Table 2 .

The previously reported impact sensitivity of sublimed SAP was studied further. The material shows no firing below 20 cm (2 kg) and the 50% level varies between 25 and 30 cm (2 kg) (50% RDX = 25 cm). The determination of SAP's sensitivity to static electrical charge is now in progress.

The storage stability tests of SAP were continued. It was previously established that SAP decomposes slowly (over 4 to 7 days) in glass containers at room temperature but is stable for as long as 1 month at -20°C. It has been found that in nickel or monel containers the material is stable for at least two months at room temperature. There is some attack of the metal surface, but the bulk of the SAP apparently remains unaffected. In Teflon containers SAP decomposes gradually within one month, but the test results have been somewhat erratic. In 320 stainless steel, there is a marked degree of decomposition within 1 month and much corrosion of the metallic surface.

Thus, the work of the past several months on the synthesis of SAP can be summarized as follows: The compound can be now readily synthesized in 2- to 3-g batches and the material is storable at room temperature in nickel or monel containers in dry atmosphere for at least several months, and probably much longer. The compound is only moderately sensitive to impact and, in this respect, does not present any handling problems. The preliminary testing data indicates that SAP is not sensitive to static electrical charge and a more thorough study of this property is now in progress. If the results of this latter testing confirm our preliminary findings, SAP can be synthesized in much larger batches using only nominal safety precautions.

As pointed out on several occasions in earlier reports, SAP represents a unique NF compound certainly of theoretical and potentially of practical importance. The determination of its heat of formation, therefore, would be of utmost importance, and arrangements have been made with Mr. Fasolino of the National Research Corporation to study SAP on their Office of Naval Research program.

2. Experimental

Purification of Fluorammonium Perchlorate

A column of 22-mm internal diameter provided with a Teflon stopcock was packed with a suspension of silica gel in ethyl acetate. The adsorbent (grade 12, 28 to 200 mesh) was activated by heating for 18 hours at 185°C. A solution of 1.85 g of crude SAP (containing 1.85% C) in 10 ml ethyl acetate was introduced into the column over a period of 37 minutes. The column was then washed with 55 ml of fresh solvent. Elution took place at the rate of about 1.7 ml/min. Most of the solvent was removed from the solution under reduced pressure, leaving a solution of 6- to 8-ml volume. Dilution with about 3 volumes of chloroform caused precipitation of the product which was separated by filtration, washed well with chloroform, and dried overnight under vacuum. The colorless product weighed 1.17 g.

Anal. Found: C, 0.22.

III. PERSONNEL

The experimental work was performed by K. Baum, V. Grakauskas, H. Marcus, M. P. Mascari, A. H. Remanick, and O. S. Schaeffler. Analytical support was provided by C. L. Deuel (gas chromatography), K. Inouye (microanalyses), and H. Nelson (IR and NMR).

TABLE 1

X-RAY DIFFRACTION PATTERN OF FLUOROAMMONIUM PERCHLORATE

$d^{\circ}A$	I/I_o	$d^{\circ}A$	I/I_o
9.60	w	3.11	s
8.26	vw	29.3	w
7.53	w	2.78	vw
6.70	vvw	2.63	w
6.23	vvw	2.53	w
5.26	m	2.45	2
4.82	wm	2.29	vw
4.09	w	2.18	vw
3.64	m	1.95	vw
3.43	m	1.82	w
3.29	w		

TABLE 2

SOLUBILITY OF FLUOROAMMONIUM PERCHLORATE

Key: i, insoluble; d, soluble with decomposition; s, soluble

Solvent	Behavior of Fluoroammonium Perchlorate
Nitrobenzene	i
1,2-dichlorobenzene	i
Cyclohexane	i
Benzene	i
Chloroform	i
Carbon tetrachloride	i
Diisopropyl ether	d
Ethanol	d
Methanol	d
Ethyl acetate	s
Amyl acetate	s
Tetrahydrofuran	s
Monoglyme	s
Acetonitrile	s

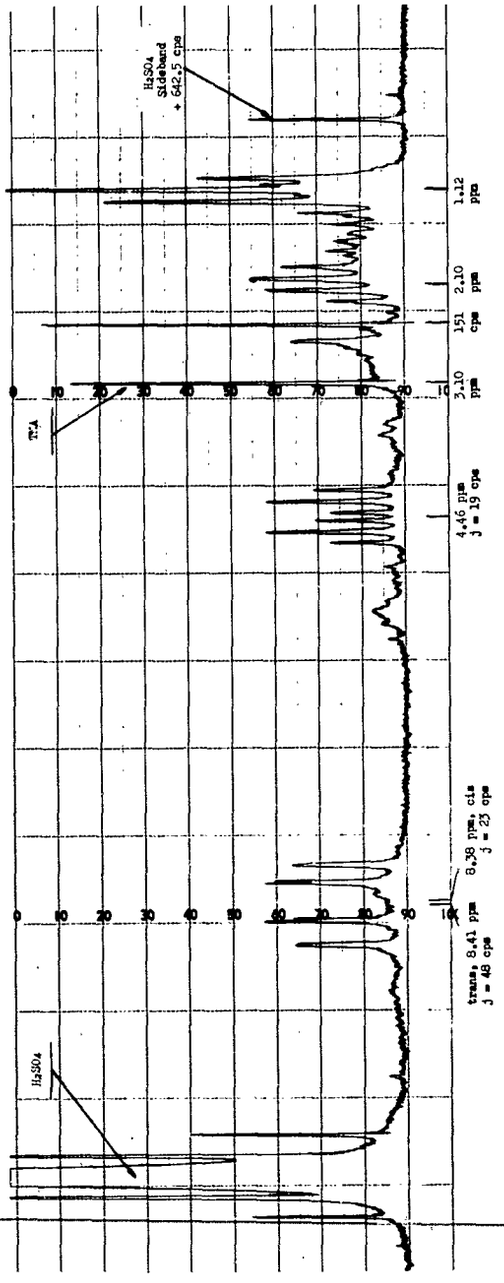


Fig. 1. Proton NMR Spectrum of 1-Difluoraminobutane Rearrangement Product

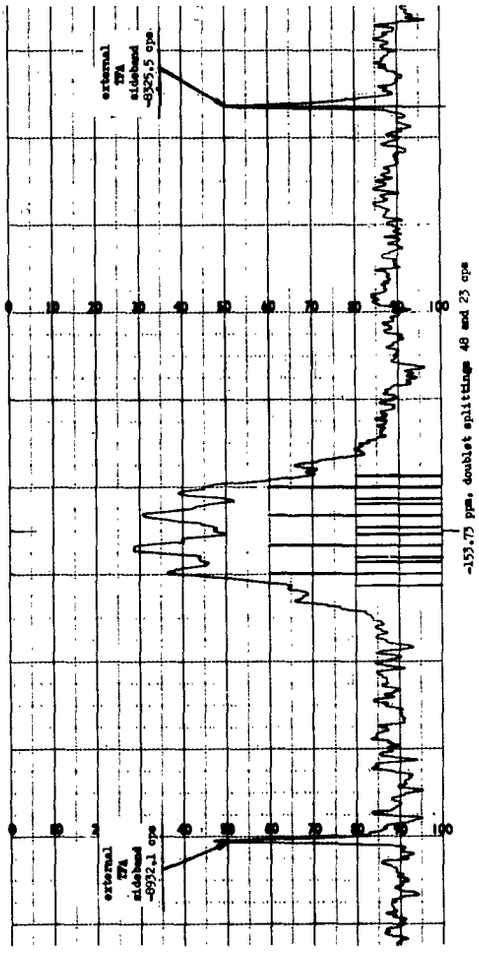


Fig. 2. Fluorine NMR Spectrum of 1-Difluoraminobutane Rearrangement Product

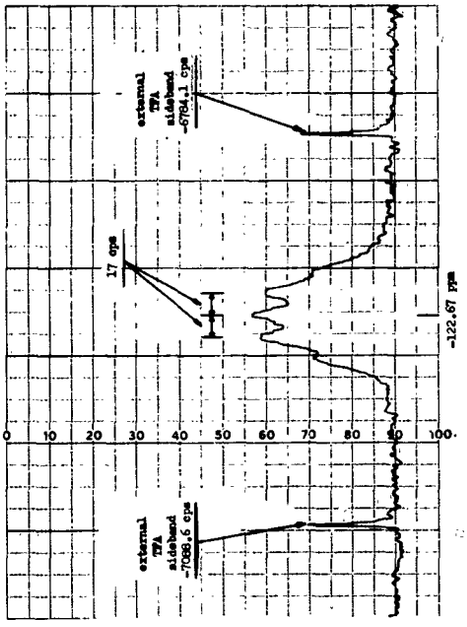


Fig. 3. Fluorine NMR Spectrum of 2-Difluoraminobutane Rearrangement Product

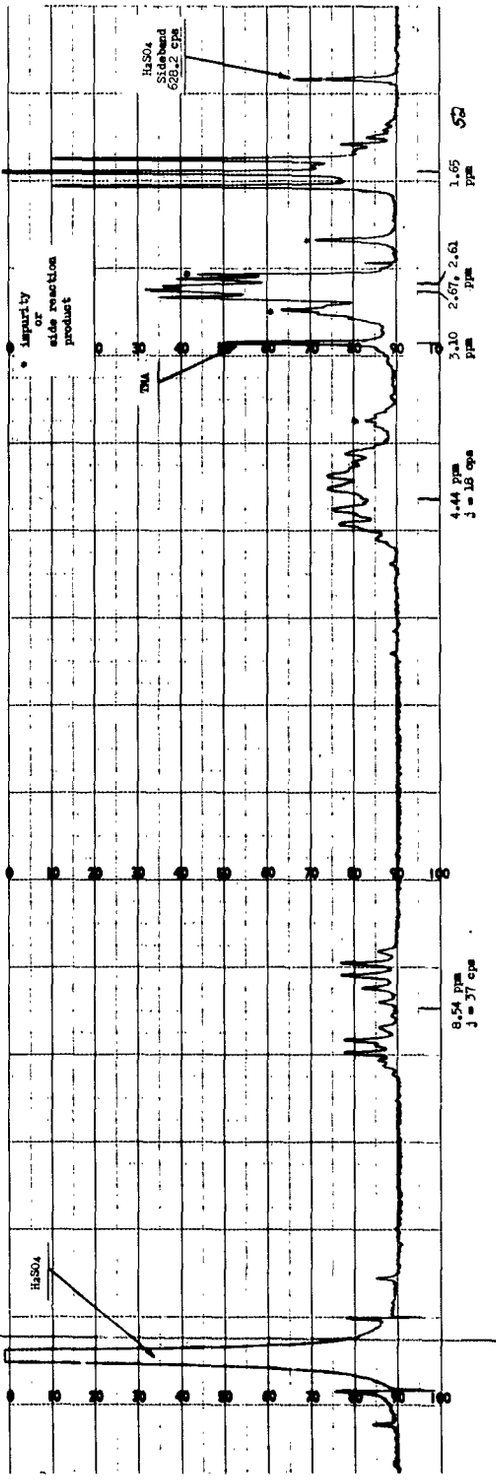


Fig. 4. Proton NMR Spectrum of 2-Difluoraminobutane Rearrangement Product

Fig. 5. Proton NMR Spectrum of 2-Difluoraminobutane Rearrangement Product (2.5 to 3.1 ppm)

Fig. 6. Infrared Spectrum of α-Bromo-α-fluoriminotoluene

Figures 5 and 6

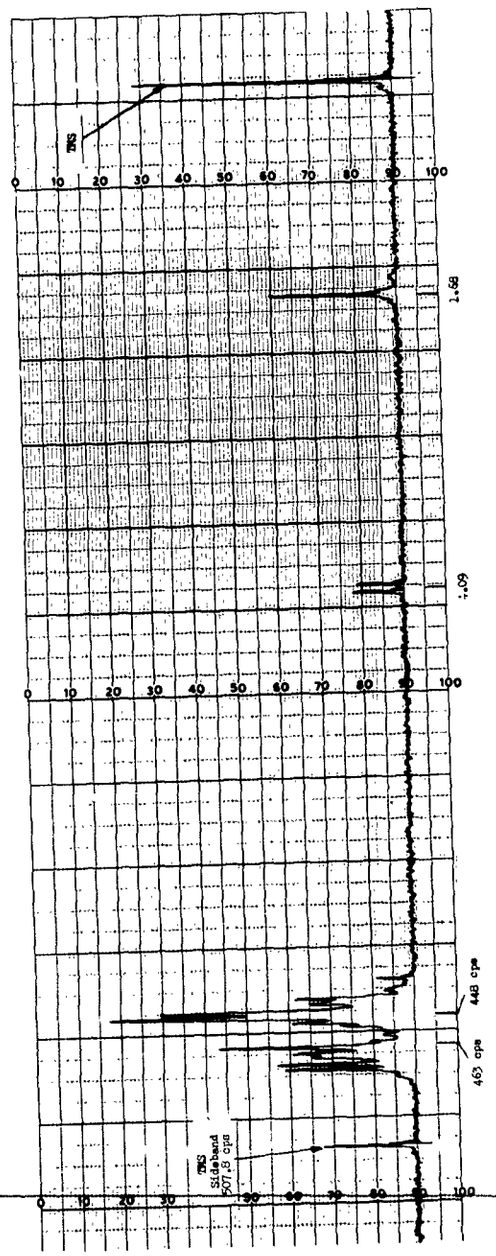


Fig. 7. Proton NMR Spectrum of α-Bromo-α-fluoriminotoluene

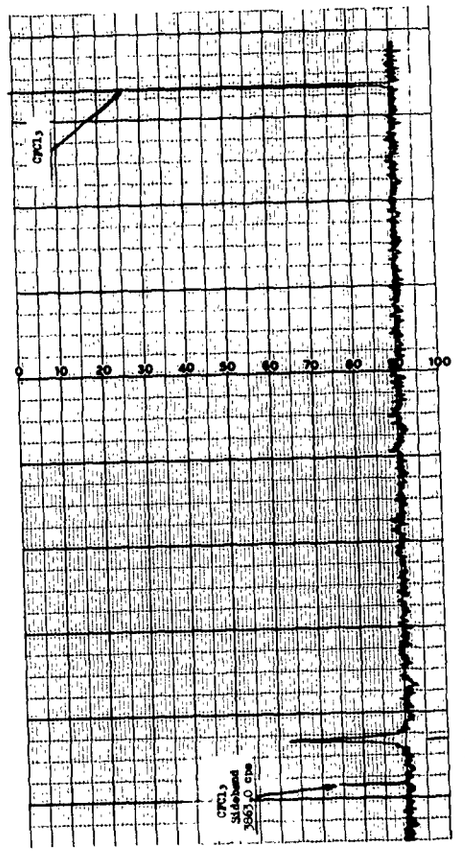


Fig. 8. Fluorine NMR Spectrum of α-Bromo-α-fluoriminotoluene

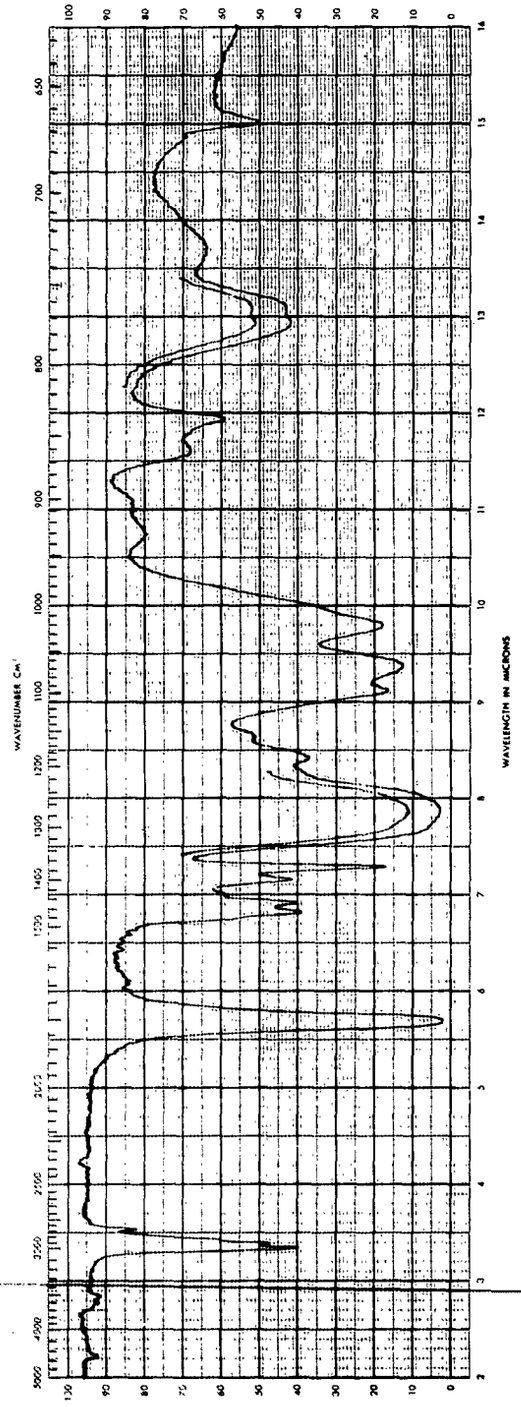


Fig. 9. Infrared Spectrum of N,N'-DImethoxy-N,N'-dicarbethoxyhydrazine

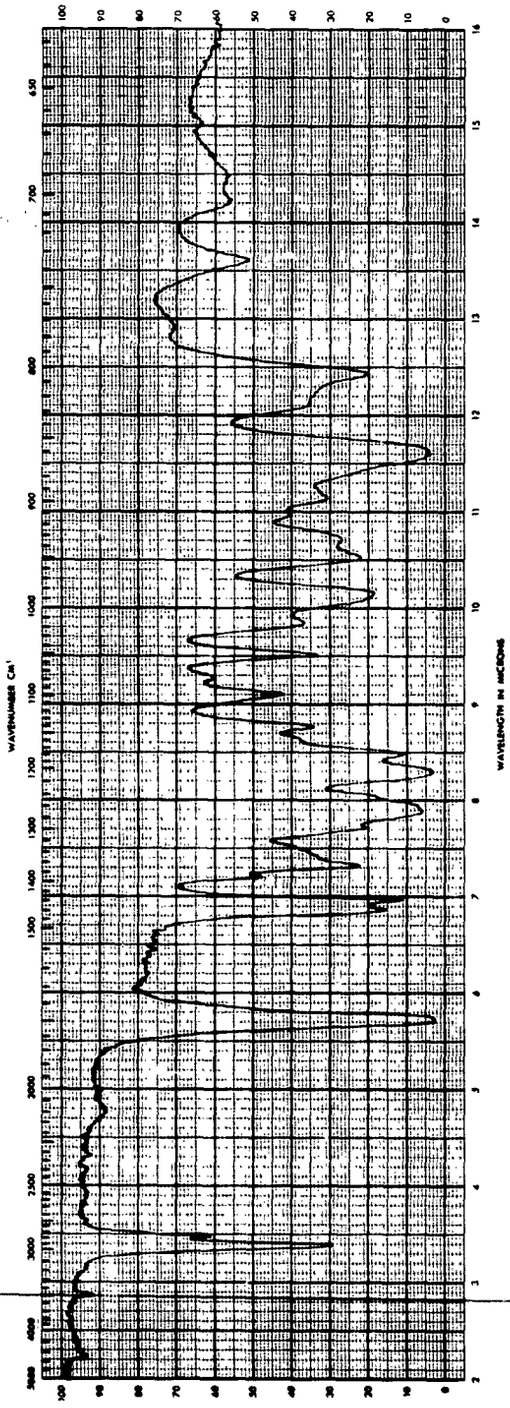


Fig. 10. Infrared Spectrum of Methyl α-Difluoraminobutyrate

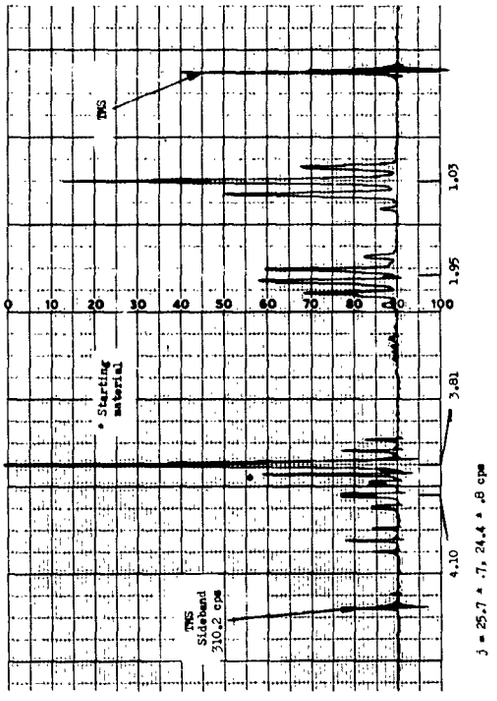


Fig. 11. Proton NMR Spectrum of Methyl α-Difluoraminobutyrate

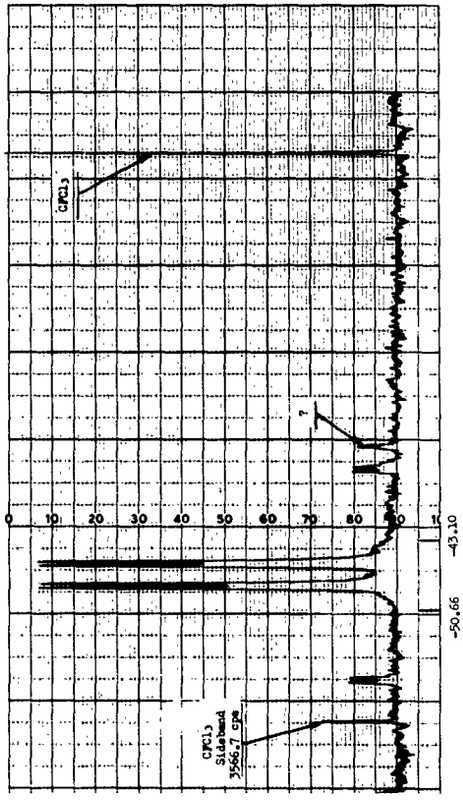


Fig. 12. Fluorine NMR Spectrum of Methyl α-Difluoraminobutyrate

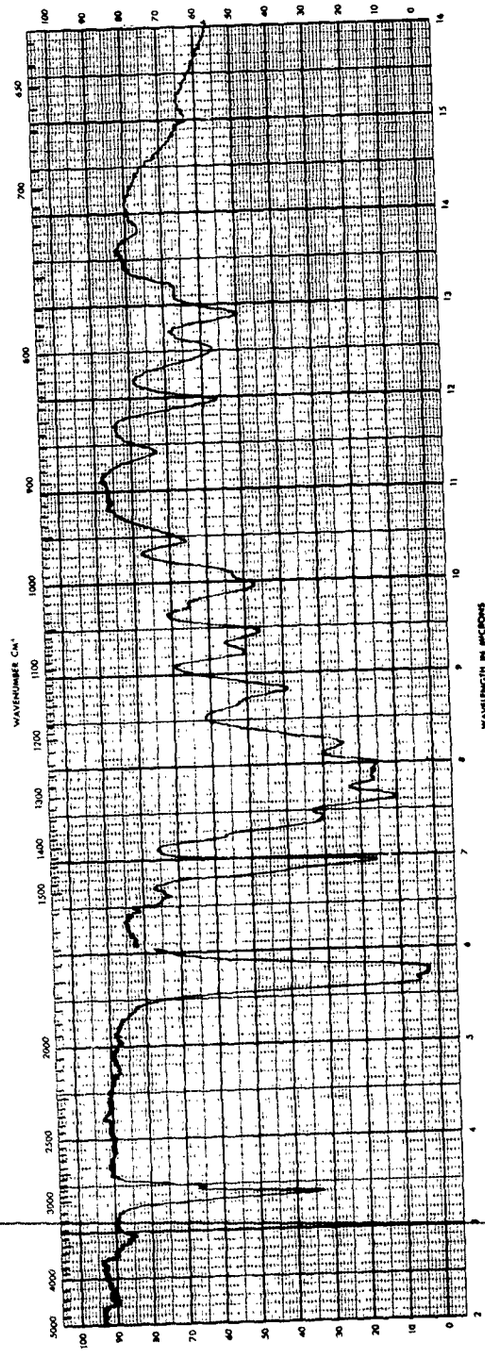


Fig. 13. Infrared Spectrum of Methyl α-(N-carbomethoxy-N-fluoro)aminobutyrate

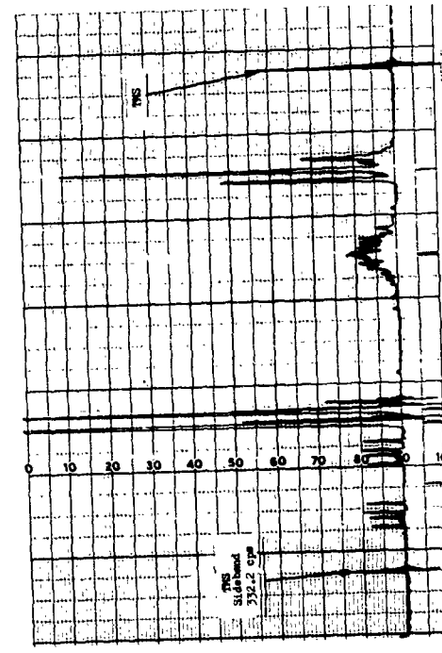


Fig. 14. Proton NMR Spectrum of Methyl α-(N-carbomethoxy-N-fluoro)aminobutyrate

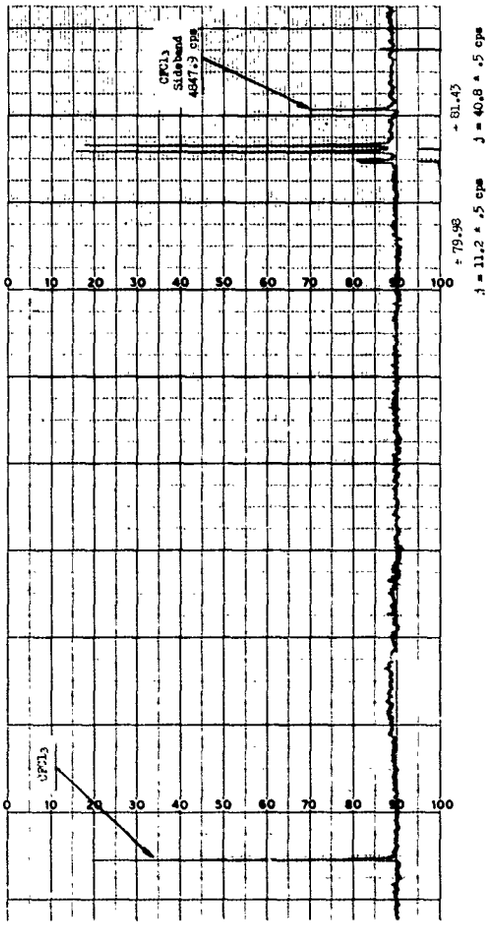


Fig. 15. Fluorine NMR Spectrum of Methyl α-(N-carbomethoxy-N-fluoro)aminobutyrate

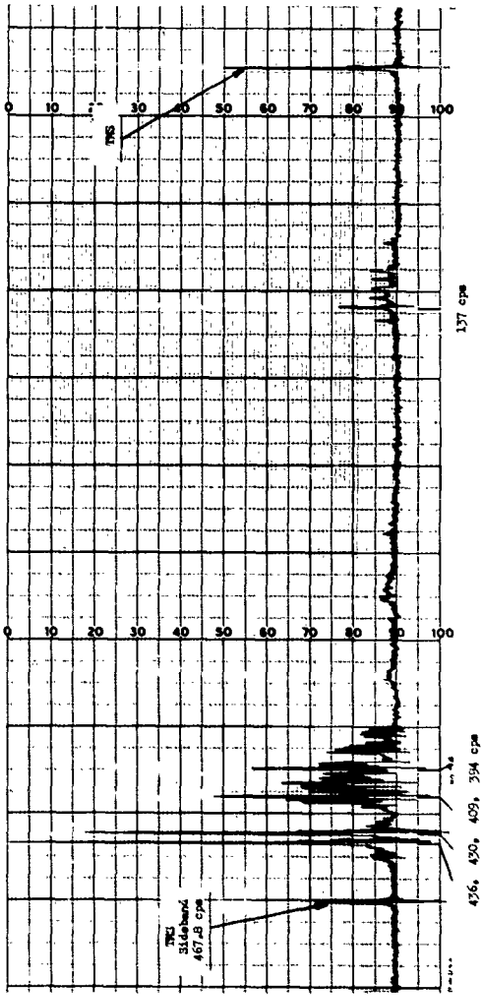


Fig. 16. Proton NMR Spectrum of 2,4,6-Trichloroaniline Fluorination Product

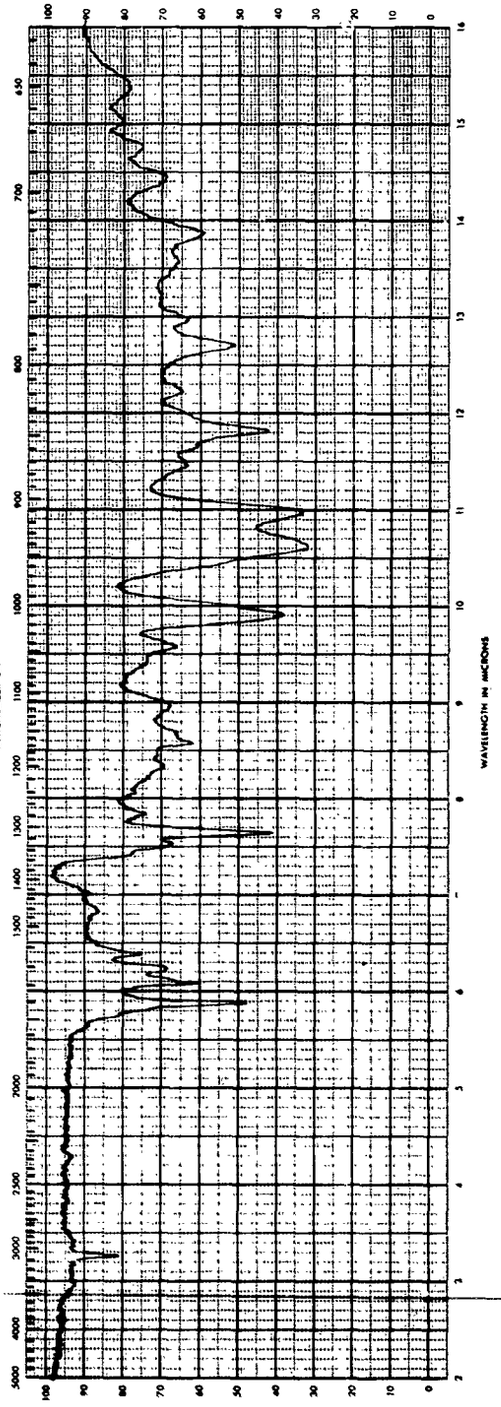


Fig. 17. Infrared Spectrum of 2,4,6-Trichloroaniline Fluorineation Product

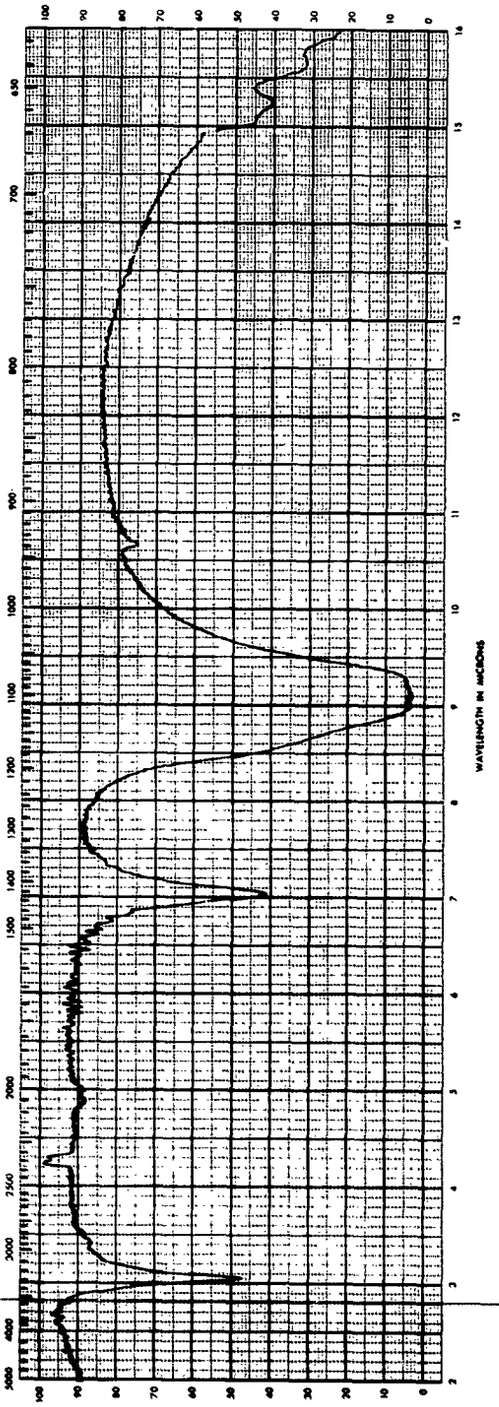


Fig. 18. Infrared Spectrum of Fluoroammonium Perchlorate

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