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REPORT NO. 3132 (SUMMARY)

PERIOD COVERED: 1 OCTOBER 1964 - 30 SEPTEMBER 1965

**RESEARCH IN FLUORO-NITRO
COMPOUNDS (U)**

A REPORT TO

OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

CONTRACT Nonr 2652(OC)

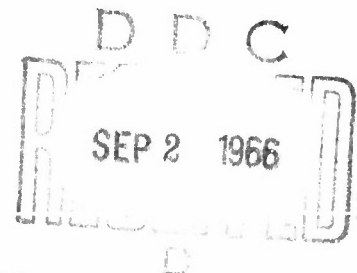
ARPA ORDER NO. 170, AMENDMENT NO. 6

PROJECT CODE 4910

AUGUST 1966

COPY NO.

CP-11-10



CHEMICAL AND STRUCTURAL PRODUCTS DIVISION
AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

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August 1966

Report No. 3132
(Summary)

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

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A Report to

OFFICE OF NAVAL RESEARCH
and
ADVANCED RESEARCH PROJECTS AGENCY

Contract NONr 2655(00)
ARPA Order No. 170, Amendment No. 7
Project Code 4910

Research reported in this publication was supported by the Advanced Research Projects Agency.

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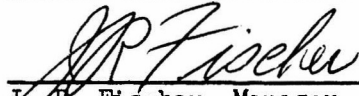
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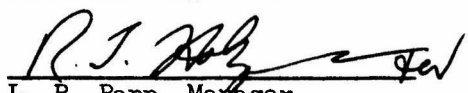
Report No. 3132

CONTRACT FULFILLMENT STATEMENT

This report summarizes the research carried out under Contract Nonr 2655(00), ARPA Order No. 170, Amendment No. 7, Project Code 4910, during the period 1 October 1964 through 30 September 1965.

AEROJET-GENERAL CORPORATION


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Report No. 3132

ABSTRACT

During the past year, work was continued on studies of the reactions of difluoramine and on direct fluorination of nitrogenous compounds in solution with the objective of synthesizing new types of high-energy NF compounds. Chemical and physical properties of new compounds were examined. Work was also continued on the preparation, isolation, and characterization of fluoro-ammonium salts.

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I. INTRODUCTION

This report summarizes the research carried out under Contract NOnr 2655(00) during the period 1 October 1964 through 30 September 1965. The work performed from 1 October 1964 through 30 June 1965 has been reported in Aerojet Quarterly Report Nos. 0235-01-21, -22, and -23; these will be summarized and referenced in this report. Experimental details will be included in the present report only for the period 1 July 1965 to 30 September 1965; the work of this period is a direct continuation of the research under Contracts NOnr 2655(00) and N7onr-462, Task Order 1, which has been summarized in Aerojet Report Nos. 1163, 1318, 1509, 1685, 1877, 2099, 2381, 2730, and 2945.

During the past year, research was continued on the reactions of difluoramine and solution fluorinations, with the objective of developing general methods for preparing more energetic compounds, and obtaining a more thorough understanding of the reactions involved. Work was also continued on the preparation and characterization of fluoroammonium perchlorate, for the purpose of enabling larger scale production of this novel oxidizer.

II. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINE (K. Baum)

1. Introduction

Efforts were continued to find a general synthesis of 1,1,1-tris(difluoramino)alkanes. Although this result was not attained, novel intermediates were isolated and their chemical properties were studied. Reactions of general classes of difluoraminoalkanes with strong acids were also studied, with results pertinent to the synthesis of high-energy compounds by difluoramine reactions.

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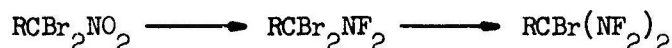
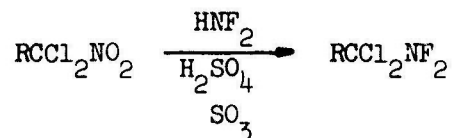
II Technical Discussion, A (cont.)

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2. Discussion

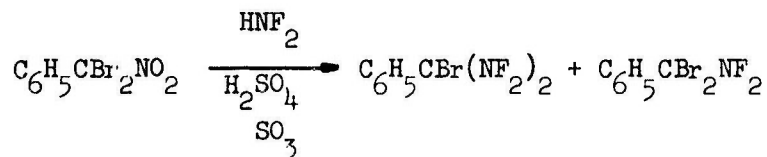
a. Reactions of Halo and Nitro and Nitroso Compounds with Difluoramine

It was previously shown that terminal dichloronitroalkanes underwent replacement of nitro groups by difluoramine in fuming sulfuric acid to give α,α -dichlorodifluoramines, and that terminal dibromonitroalkanes underwent the analogous reaction with subsequent replacement of a bromine atom.*



Attempts to affect further replacement of halogens to yield a 1,1,1-tris(difluoramino)-alkane was unsuccessful.

Subsequent work** was done with benzylic systems, since the activation of the halogens by the aromatic ring would increase the probability of complete replacement. The reaction of α,α -dibromo- α -nitrotoluene with refluxing difluoramine in fuming sulfuric acid thus gave a mixture of α -bromo- α,α -bis(difluoramino)toluene and α,α -dibromo- α -difluoraminotoluene. (Attempts to produce further reaction under more forcing conditions were unsuccessful.)



A similar reaction of bromopicrin with difluoramine would be expected to give tribromo(difluoramino)methane or subsequent bromine replacement products. When this reaction was conducted at atmospheric pressure, at the reflux temperature of difluoramine, for 4 hours, only the starting material was recovered:

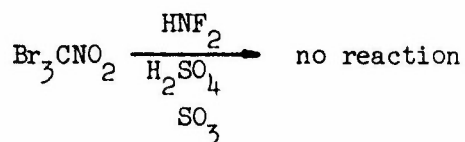
*Aerojet Report No. 2945, October 1964 (Confidential).

**Aerojet Report No. 0235-01-21, February 1965, p. 1 (Confidential).

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II Technical Discussion, A (cont.)

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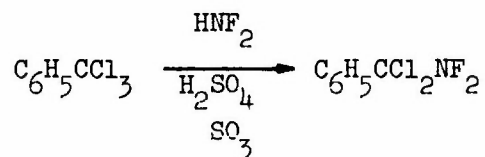


Again, when the reaction was attempted at ambient temperature and autogenous pressure for 20 hours, no reaction took place. It was thought that the lack of reactivity might be the result of the insolubility of bromopicrin in the reaction medium. Consequently, the reaction at atmospheric pressure was repeated, with the addition of enough nitromethane to give a homogeneous solution. Only nitromethane and bromopicrin were recovered. This technique was not attempted in a room temperature reaction because a mixture of fuming sulfuric acid and nitromethane is unstable under these conditions.

An unsuccessful attempt also was made to react difluoramine with the self-condensation product of dinitroethane, ^{*} $\text{CH}_3-\text{C}(\text{NO}_2)=\text{N}-\text{OC}(\text{NO}_2)_2\text{CH}_3$ or $\text{CH}_3-\text{C}(\text{NO}_2)=\text{N}-\text{C}(\text{NO}_2)_2\text{CH}_3$. No reaction took place when fuming sulfuric acid and re-

fluxing difluoramine were used. This failure to react is surprising, since one nitro group of this compound is readily replaced by HCl and alcohols.

The reaction of α,α,α -trichlorotoluene with refluxing difluoramine in fuming sulfuric acid gave α -difluoramino- α,α -dichlorotoluene, but no higher substitution products.



Since secondary α -halo-nitro compounds have been shown to react readily with difluoramine in sulfuric acid to give gem-difluoramines,

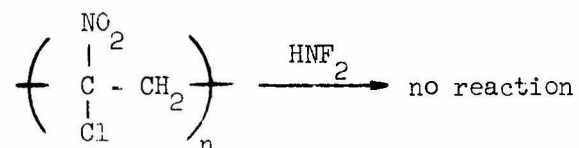
^{*} J. S. Belew, C. E. Grabiell and L. B. Clapp, "Reaction of 1,1-Dinitroethane with Its Salts," J. Am. Chem. Soc., **77**, 1110 (1955).

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II Technical Discussion, A (cont.)

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an attempt was made to apply this reaction to the preparation of a high-energy polymer. 1-Chloro-1-nitroethylene was prepared by a modification^{*} of the method of Wilkendorf and Trenel,^{**} and was polymerized by contact with aqueous sodium bicarbonate. The polymer, however, was insoluble in the difluoramine-fuming sulfuric acid reagent, and was recovered largely unchanged after a 4 hour reaction period at atmospheric pressure. The substitution of flusulfonic acid for the fuming sulfuric acid gave the same results.



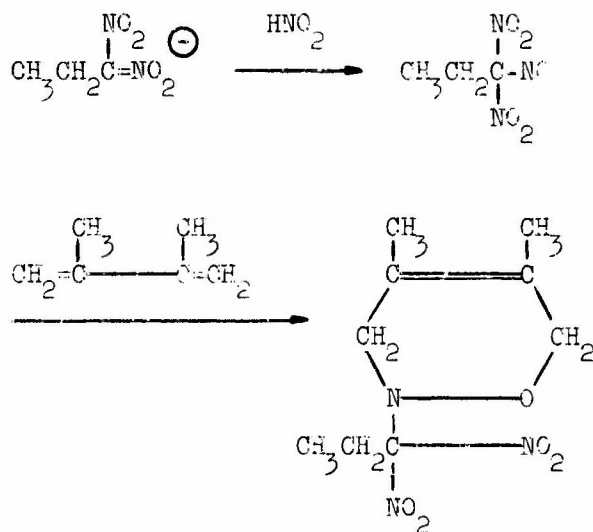
1-Halo-1-nitro-1-nitrosoalkanes have been shown to undergo replacement of nitro and nitroso groups by difluoramino groups in the reaction with difluoramine in sulfuric acid. Efforts were made^{***} to apply this reaction to 1,1-dinitro-1-nitrosoalkanes, a previously unreported class of compounds. The nitrosation of the sodium salt of 1,1-dinitropropane at 0°C in aqueous solution resulted in the precipitation of a dark-blue oil. However, the material was too unstable for purification by distillation; a sample kept at room temperature decomposed within about 30 min. The structure of the product was demonstrated by adding 2,3-dimethyl-1,3-butadiene to a freshly prepared sample. The crystalline Diels-Alder adduct, isolated in 71.5% yield, was characterized by elemental analysis.

^{*}Aerojet Report No. 0235-01-23, August 1965, p. 3 (Confidential).
^{**}R. Wilkendorf and M. Trenel, Ber., 57, 308 (1924).
^{***}Aerojet Report No. 2945, October 1964, p. 1 (Confidential).

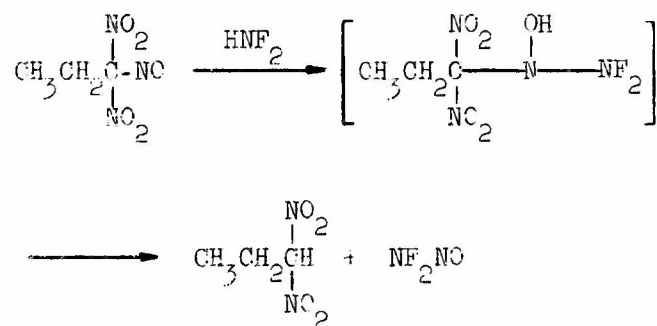
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II Technical Discussion, A (cont.)

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The reaction of a freshly prepared sample of 1,1-dinitro-1-nitrosopropane with difluoramine was carried out, using 20% fuming sulfuric acid as the catalyst. When the reaction mixture was quenched, extracted, and distilled, a 45% yield of 1,1-dinitropropane was obtained. No other product was isolated. Apparently, the inductive effect of the two nitro groups is sufficient to prevent the formation of a carbonium ion, so that the nitroso compound acts as a nitrosating agent toward difluoramine. An addition compound may be an intermediate.



This reaction course has been reported for the reaction of 1-nitro-1-nitrosocyclohexane, in addition to the alternative mode of cleavage leading to the gem-difluoramine.*

* Aerojet Report No. 0235-01-20, July 1964, p. 2 (Confidential)

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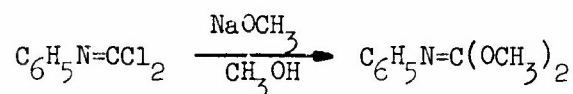
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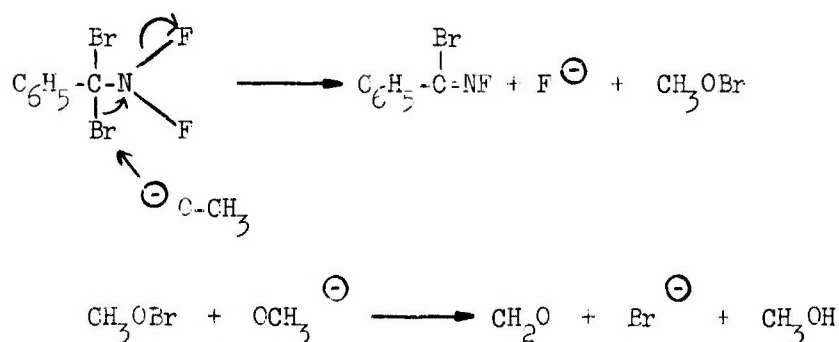
b. Chemical Properties of α -Halodifluoramines

The three above difluoramino-toluenes, because of their ready availability and freedom from reactive hydrogens, were used for a brief study of the chemical properties of this class of compounds.

When α, α -dibromo- α -difluoramino-toluene was treated with methanolic sodium methoxide for 18 hours at room temperature, the product - isolated in 59% yield - was identified as dimethyl carbonate anil by means of elemental analysis, IR, and NMR spectra. Preparation of this compound by the reaction of phenyl isonitrile dichloride with sodium methoxide was reported in 1892:*



The overall reaction of α, α -dibromo- α -difluoramino-toluene with methoxide must include a reduction step, a phenyl migration, and a bromine displacement. The following mechanism rationalizes the product, but other sequences of the steps are equally logical:

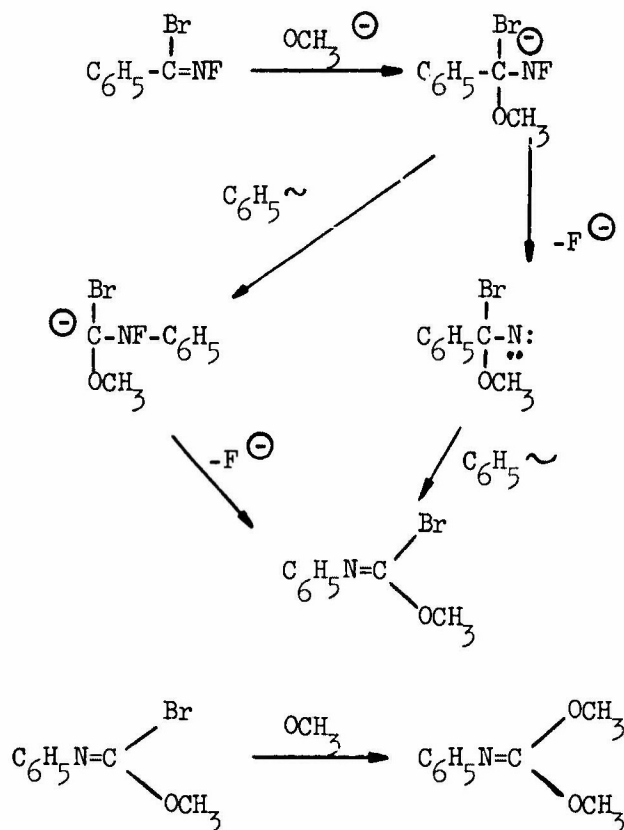


* A. Smith, J. Am. Chem. Soc., 16, 392 (1892).

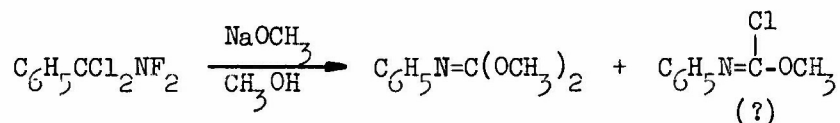
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II Technical Discussion, A (cont.)

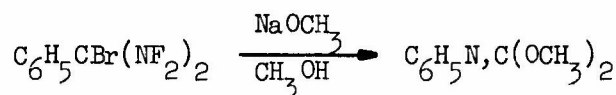
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The reaction of α,α -dichloro- α -difluoramino toluene with sodium methoxide was slower than that of the bromo compound, and required heating. Under conditions that gave conversion of only a fraction of the starting material, dimethyl carbonate anil was also formed. Another compound, not fully characterized, was present which appeared to be methyl chloroformate anil, on the basis of its NMR spectrum:



α -Bromo- α,α -bis(difluoramino)toluene also reacted with methanolic sodium methoxide to give dimethyl carbonate anil:



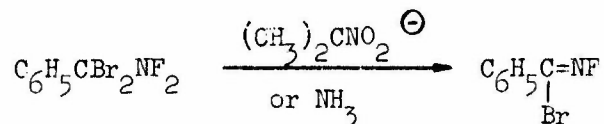
In this case a small impurity with infrared absorption at 5.80μ was also produced.

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II Technical Discussion, A (cont.)

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In the reactions of α,α -dibromo- α -difluoramino-toluene with sodium 2-propanenitronate^{*} and with liquid ammonia,^{**} α -bromo- α -fluorimino-toluene was isolated. These mild bases thus act as reducing agents toward the NF_2 group.



Some reactions of α,α -dibromo- α -difluoramino-toluene, α -bromo- α,α -bis(difluoramino)toluene, and α -difluoramino- α,α -dichlorotoluene 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 tetra-alkylguanidines corresponding to the above reactions, but elemental analyses were unsatisfactory.

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 hours, a homogeneous solution was formed. The F^{19} NMR spectrum of this solutions 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.^{***}

c. Reaction of Alkyldifluoramines with Acids

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

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

^{**} Aerojet Report No. 0235-01-23, August 1965, p. 3 (Confidential).

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

^{****} Aerojet Report No. 2945, October 1964, p. 9 (confidential).

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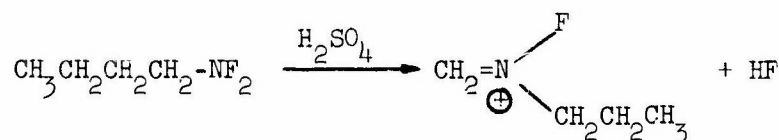
II Technical Discussion, A (cont.)

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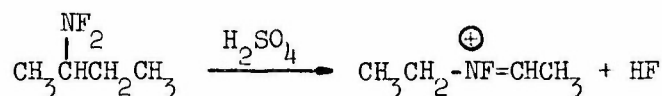


The potential usefulness of this reaction for predicting side products in difluoramine reactions prompted the investigation of other types of difluoramine compounds.

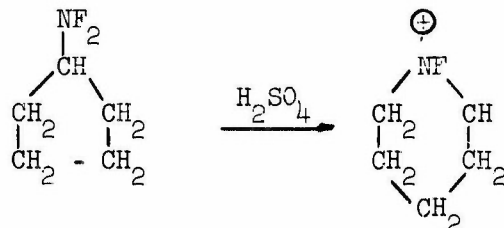
1-Difluoraminobutane^{*} reacted with concentrated sulfuric acid at 0°C when shaken to give a homogeneous solution. The H¹ and F¹⁹ NMR spectra of this solution were consistent with the propyl migration product, N-fluoro-N-propylmethylenimmonium ion.



2-Difluoraminobutane reacted under the same conditions to give the ethyl migration product, N-fluoro-N-ethylethylidenimmonium ion, which was identified by the NMR spectra of the sulfuric acid solution.^{**} The product hydrolyzed to some extent while the spectrum was being run, but the interfering peaks were largely eliminated by rapidly running only that portion of the spectrum using a fresh sample.



Cyclopentylidifluoramine reacted as expected with sulfuric acid to give the cyclic imonium ion.^{***}



^{*}Aerojet Report No. 0235-01-22, May 1965, p. 2 (Confidential).
^{**}Aerojet Report No. 0235-01-22, May 1965, p. 3 (Confidential).
^{***}Aerojet Report No. 0235-01-23, August 1965, p. 3 (Confidential).

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II Technical Discussion, A (cont.)

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The migratory aptitudes observed in the rearrangement of alkyldifluoramines are consistent with those in other rearrangements to electron-deficient centers, in which the migrating group tends to be the one best able to support a positive charge. Thus, in the 2-difluoramino-butane reaction, the ethyl group migrates in preference to the methyl. The propyl group of 1-difluoramino-butane migrates readily, while the methyl group of ethyldifluoramine does not. The migration of the methyl group in *t*-butyldifluoramine, on the other hand is facilitated by the carbonium ion stabilization of the non-migrating

methyl groups, rendering the contribution of $(\text{CH}_3)_2\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}=\text{NF}$ less important in the transition state, compared to $(\text{CH}_3)_2\overset{\text{CH}_3}{\text{C}}-\text{NF}$. This general effect has been discussed in a paper by Berson and Suzuki on the Baeyer-Villiger rearrangement.*

Because a large amount of work has been reported in which N_2F_4 adducts of functionally substituted olefins were used as starting materials for acid-catalyzed difluoramine reactions, it was decided to determine the reactivity of a simple N_2F_4 adduct with acids. 1,2-Bis(difluoramino)-hexane was selected as a model compound with convenient physical properties.

The compound selected was found to react with concentrated sulfuric acid at 0° , with agitation, to form a clear solution. The NMR spectra of the solution, however, were quite complex, and changes in peak height took place while the spectra were being run. Thus, although rearrangement or hydrolytic degradation of the difluoramino groups obviously took place, the nature of the reactions could not be determined.

Fluosulfonic acid, another commonly used catalyst for difluoramine reactions, was also tested for reactivity with 1,2-bis(difluoramino)-cyclohexane. At 0°C , the reaction was quite violent. However, when the bis(difluoramino)cyclohexane was added to fluosulfonic acid at -80° , the two liquids were immiscible, but a clear solution resulted after the mixture was agitated gently for several minutes. The solution was stable at room temperature and its NMR spectra did not change over a 24-hour period.

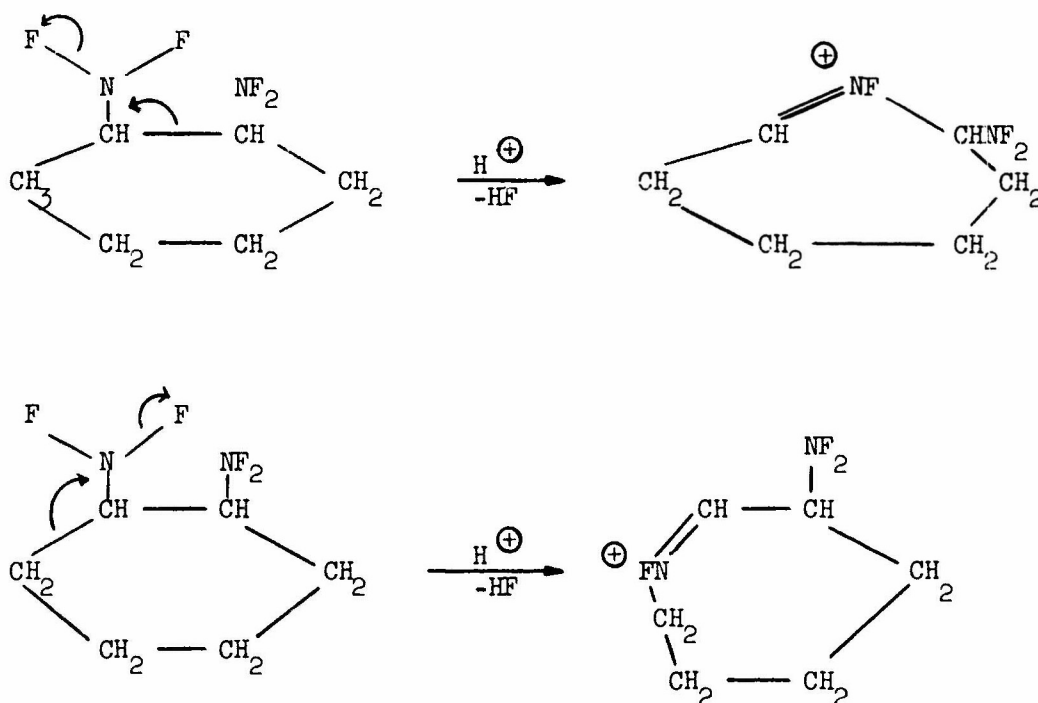
* J. A. Berson and S. Suzuki, J. Am. Chem. Soc., 81, 4088 (1959).

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II Technical Discussion, A (cont.)

Report No. 3132

Rearrangement by the same mechanism as that of the simple alkyl difluoramines would result in the rupture of either the CHNF_2 - CHNF_2 bond or the CHNF_2 - CH_2 bond, as follows:



The NMR spectra of the fluosulfonic acid solution are consistent with the latter reaction course. The proton spectrum (Figure 1) thus contains a doublet of doublets at 9.4 ppm, representing the "olefinic" proton coupled with a proton ($j = 3.7$ cps) and one fluorine ($j = 25.6$ cps). The doublet at 4.7 ppm is assignable to the methylene α to the nitrogen, coupled (18 cps) to the NF_2 , and the broad peak at 2.2 ppm is assigned to the remaining ring protons. The F^{19} spectrum (Figure 2) shows an AB quartet with components at -132.5 and -119.0, indicating CHNF_2 , and a broadened peak at -179.4 ppm representing the $=\text{N}-$.

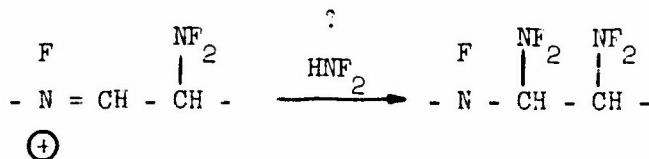
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The addition of difluoramine to an imonium ion such as that above could provide a general means of upgrading NF content.



An attempt was made to affect this reaction by adding difluoramine to a fluosulfonic acid solution of the rearrangement product of 1,2-bis(difluoramino)-hexane. Workup, however, gave an uncrystallizable oil which decomposed during an attempted distillation.

3. Experimental

a. Reaction of 1,2-bis(Difluoramino)cyclohexane with Fluosulfonic Acid

1,2-Bis(difluoramino)cyclohexane was prepared by the addition of tetrafluorohydrazine to cyclohexene.* A stoppered test tube containing 1-ml of fluosulfonic acid was cooled in a -80° bath and 0.2 ml of 1,2-bis(difluoramino)cyclohexane was added. The two liquids were initially immisable, but after the test tube immersed in coolant was shaken for several minutes, a solution was formed. The NMR spectra of this solution are shown in Figures 1 and 2. Chemical shifts of the proton spectrum are referred to tetramethylsilane, through the use of tetramethylammonium ion as an internal standard. The reference for the F^{19} spectrum is external trifluoroacetic acid.

b. Reaction of 1,2-Bis(difluoramino)cyclohexane Rearrangement Product with Difluoramine

To 30-ml of fluosulfonic acid cooled to -80° , 3.0 gram of 1,2-bis(difluoramino)cyclohexane was added dropwise, with stirring. Stirring was continued until solution was completed. This solution was placed in a difluoramine reactor. Approximately 27 g of difluoramine was generated from difluorourea and was allowed to reflux over the above solution for 3.5 hours. The

*Thiokol Report RMD-ACR-ATS-63, "Advanced Oxidizer Research" (Confidential).

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II Technical Discussion, A (cont.)

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solution was quenched over ice and was extracted with three 30 ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and the solvent was removed. The infrared spectrum of the residue indicated that it was a complex mixture. An attempted vacuum distillation resulted in charring.

c. Reaction of Polychloronitroethylene with Difluoramine

To a refluxing mixture of 27 g of difluoramine and 15 ml of 20% fuming sulfuric acid, 3.2 g of the polymer of 1-chloro-1-nitroethylene was added. The addition was accomplished by placing the polymer, before the difluoramine was generated, in a bent standard-taper tube fitted to the reaction flask. The polymer was added to the refluxing reagent then by remotely twisting the tube upright. The mixture was stirred at the reflux temperature of difluoramine for 4.5 hours. After this period, insoluble solid was still present. Difluoramine was vented off and the mixture was poured over ice. The ice was melted, and the insoluble solid was filtered, washed with water and dried under vacuum. The infrared spectrum of the solid was almost identical to that of the starting material.

A similar experiment using fluosulfonic acid as the catalyst gave the same result.

B. DIRECT FLUORINATION (V. Grakauskas)

1. Introduction

During the past year, the liquid phase fluorination of nitrogenous compounds was studied exclusively in nonaqueous solvents, capitalizing on earlier findings which indicated that (in many cases) better yields of NF compounds could be obtained under these reaction conditions than in aqueous fluorination. The anticipation that more energetic NF compounds could be synthesized under these conditions^{*} was realized during the last two quarters of this year when it was found that fluorination of guanidine derivatives resulted in selective replacement of hydrogens by fluorine without the fragmentation of substrate molecules.

a. Amides, Carbamates, and Ureas

The solution fluorinations of simple sec. amides, carbamates, and ureas were studied as models for more energetic systems and as

^{*} Aerojet Report No. 2945 (Summary), October 1964, p. 14 (Confidential).

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II Technical Discussion, B (cont.)

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sources of reaction intermediates. As no further work is contemplated in this area, earlier results will be summarized in addition to last year's work.

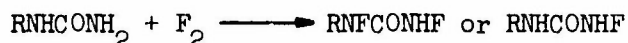
The fluorination of alkylcarbamates and sec.-amides proceeds stepwise to give first the corresponding N-fluoro derivatives which on further fluorination yield alkyldifluoramines:



X = alkyl or alkoxy group

In Aerojet's early work, these reactions were studied in aqueous solution and yields of NF compounds were relatively low, ranging between 15 and 40%. Subsequently, the yields were increased to the 40 to 70% range by fluorinating in nonaqueous solvents, such as methyl formate or acetonitrile.* More recently fluorination of methyl N-sec.-butylcarbamate** and ethyl N-carbomethoxyglycine*** in acetonitrile also gave high yields of NF compounds.

The rates of fluorination of alkylcarbamate**** and N-alkyl-amides***** , and of their N-fluoro derivatives, must be of about the same order of magnitude. This conclusion is based on the fact that both N-fluoro derivatives and the corresponding difluoramines are produced at low fluorine-to-substrate ratios. Also, at the end of a fluorination run, when the molar ratio of fluorine to substrate approaches the theoretical value of 2:1, the reaction mixture usually still contains some starting material.



Thus, N-fluoro-N-n-propylurea was isolated in the fluorination of n-propylurea.*****
The final reaction products in the fluorination of an alkylurea are the corresponding

*Aerojet Report No. 2945 (Summary), October 1964, p. 13 (Confidential).
**Aerojet Report No. 0235-01-21, February 1965, p. 7 (Confidential).
***Aerojet Report No. 0235-01-22, May 1965, p. 8 (Confidential).
****Aerojet Report No. 2381 (Summary), October 1962, p. 17 (Confidential).
*****Aerojet Report No. 2945 (Summary), October 1964, p. 29 (Confidential).
*****Aerojet Report No. 2945 (Summary), October 1964, p. 14 (Confidential).

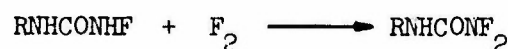
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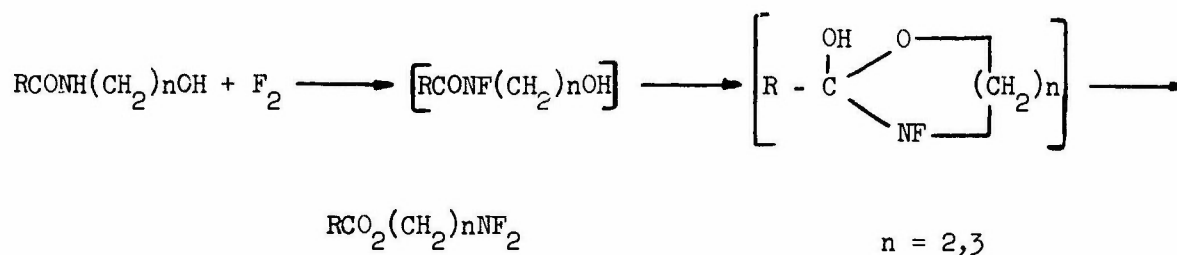
II Technical Discussion, B (cont.)

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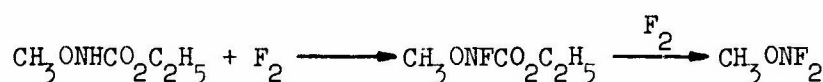
N-alkyl-N',N'-difluorourea and alkyldifluoramine, indicating that the second reaction step involves further attack on the nitrogen already carrying fluorine:



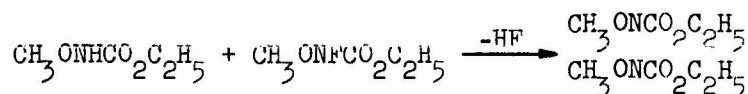
The fluorination of N-2-hydroxyethylamides* and N-3-hydroxypropylamides** gave the corresponding ω-difluoraminoalkyl esters, apparently via cyclic hemiacetal intermediates:



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:



Neither compound was obtained. The reaction product was identified as N,N'-dimethoxy-N,N'-dicarboethoxyhydrazine and the compound apparently was formed in a coupling reaction between the substrate and its N-fluoro derivative:



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

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

*** Aerojet Report No. 0235-01-22 (Quarterly), May 1965, p. 7 (Confidential).

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II Technical Discussion, B (cont.)

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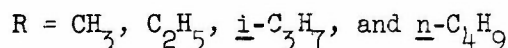
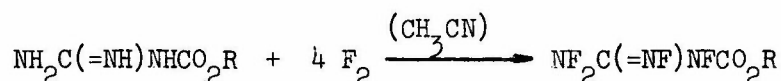
The fluorination of amides, carbamates, and ureas probably involves electrophilic attack of elementary fluorine on the unshared pair of electrons on the nitrogen atom with loss of a proton or carboalkoxy group.

b. Oximes^{*}

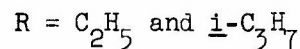
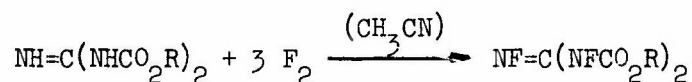
In aqueous solution, both n-butyraldioxime and acetaldioxime readily consumed fluorine, but the crude reaction product was distilled over a wide range of temperature and underwent partial decomposition with the elimination of hydrogen fluoride. Only the corresponding nitriles (5 to 10% yield) were identified among the reaction products. Similar difficulties with the identification of products were encountered when these oximes were fluorinated either in the absence of a solvent or in acetonitrile solution.

c. Guanidine Derivatives^{**}

The fluorination of 1-carboalkoxyguanidines in acetonitrile solution at 4:1 molar ratio of fluorine to substrate gave the corresponding tetrafluoro derivatives (1-carboalkoxyperfluoroguanidines):



The fluorination of 1,3-dicarboalkoxyguanidines under similar conditions at 3:1 molar ratio of fluorine to substrate gave the corresponding trifluoro derivatives (1,3-dicarboalkoxyperfluoroguanidines) in 40 to 50% yields:



* Aerojet Report No. 0235-01-21 (Quarterly), February 1965, p. 8 (Confidential).

** Aerojet Report No. 0235-01-23 (Quarterly), August 1965, p. 7 (Confidential).

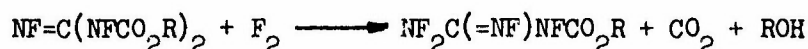
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II Technical Discussion, B (cont.)

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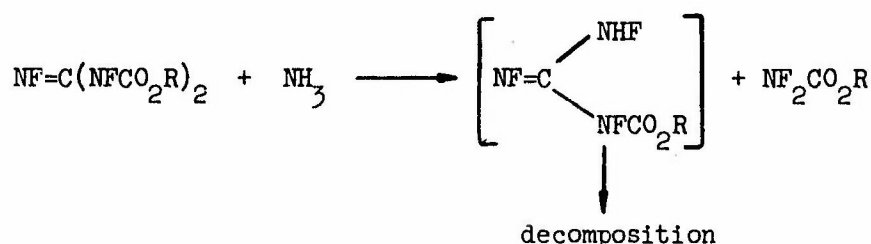
To simplify reporting, these structures will be abbreviated as C_n PFG and DC_n PFG, the C indicating 1-carboalkoxy group and De, -1,3-dicarboalkoxy groups on guanidine. The subscript indicates the number of carbon atoms in the alkyl group. Thus, C_2 PFG designates 1-carboethoxyperfluoroguanidine and DC_2 PFG, -1,3-dicarboethoxyguanidines.

In the fluorination of 1,3-dicarboalkoxyguanidines, small amounts (10 to 15%) of the corresponding CPFGs were obtained in addition to DEC-PFGs, indicating displacement of carboalkoxy group from DC-PFG:



The CPFGs and DC-PFGs are storable without noticeable decomposition at room temperature for at least several months, and appear to be relatively stable on prolonged heating at 80-100°C.

Some preliminary experiments were conducted in order to assess the reactivity of these compounds. DC_2 PFG did not react with methanol in the presence of a catalytic amount of urea either at room temperature or at 60-65°C. DC_{31} PFG was decomposed with aqueous ammonia at room temperature to give isopropyl carbamate, suggesting ammonolysis at $-NF-\overset{O}{\parallel}C-$ bond:



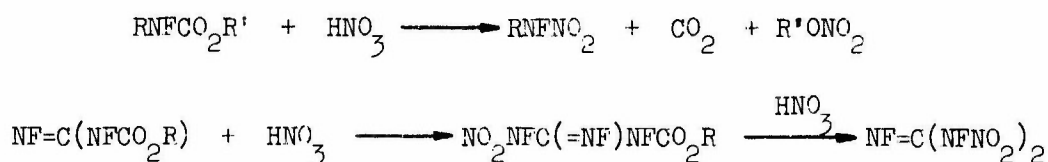
When this reaction was repeated in carbon tetrachloride solution at -25°C, using an equal molar amount of anhydrous ammonia, a mildly exothermic reaction occurred accompanied by a gradual deposition of a solid. When the reaction mixture was allowed to warm to room temperature, subsequent activity occurred, as evidenced by a slow gas evolution. At this point, the solution was analyzed by infrared and was found to contain unreacted DC_{31} PFG and isopropyl carbamate.

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By analogy to the reaction of alkyl N-alkyl-N-fluorocarbamate with 100% nitric acid,^{*} DCPFGs were expected to undergo decarboxylative nitration to give the mixed nitro-fluoroguanidines.



DC₃₁ PFG dissolved without apparent reaction in cold (10°C) 100% nitric acid. Gas evolution, accompanied by a mild exotherm began when the reaction mixture was allowed to warm to 20-25°C. Only the starting material (ca. 30% recovery) was isolated when the reaction mixture was quenched with ice water and worked up.

The fluorination of 1-carboethoxy-3-cyanoguanidine in acetonitrile solution gave a mixture of NF compounds from which three pure compounds were separated by gas chromatography. The lowest boiling component was identified as ethyl N-fluoro-N-(difluorodifluoramino)methylcarbamate, $\text{NF}_2\text{CF}_2\text{NFCO}_2\text{C}_2\text{H}_5$, on the basis of its elemental analysis and its infrared (Figure 3) and NMR spectra (see Figure 4 for F^{19} NMR spectrum). Its fluorine NMR spectrum agrees well with that of the corresponding carbamyl fluoride, $\text{NF}_2\text{CF}_2\text{NFCOF}$, reported by 3-M.^{**} The second component in the mixture was identified as ethyl N-fluoro-N-(fluorofluoramino)methylcarbamate, also on the basis of its elemental analysis and its infrared (Figure 5) and NMR spectra^{***} (see also F^{19} NMR spectrum, Figure 6). This compound may be looked upon as a derivative of perfluoroformamidine, $\text{NF}_2\text{CF}=\text{NF}$. It is interesting to note that fluorine NMR spectrum seems to indicate that the compound represents only one stereo isomer, -syn or anti. This observations is in agreement with the 3-M report^{****} on stereochemistry

*Aerojet Report No. 2351 (Summary), October 1962, p. 39 (Confidential).

**Minnesota Mining & Manufacturing Co., Chemical Research as Related to Advanced Solid Propellants, Report No. 15 (Annual), Jan-Dec., 1962, p. 59 (Confidential).

***The interpretation of fluorine NMR spectra of ethyl N-fluoro-N-(difluorodifluoramino)methylcarbamate and ethyl N-fluoro-N-(fluorofluorimino)methylcarbamate represents an interesting piece of spectroscopic work (see Experimental). The expected fluorine-to-fluorine couplings not showing in the "normal" spectra were found in decoupling experiments.

****Op.cit., p. 65.

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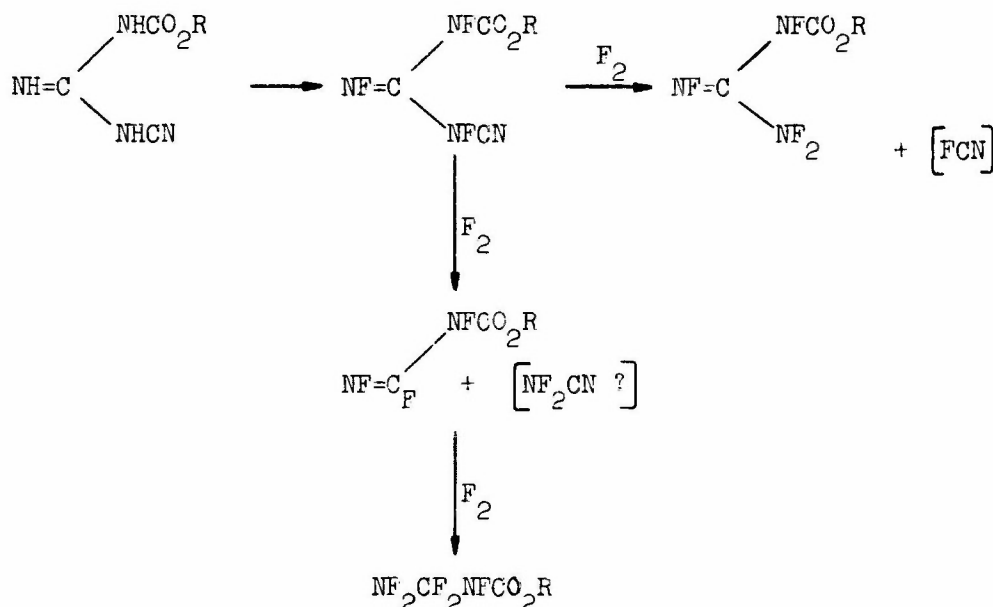
II Technical Discussion, B (cont.)

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of perfluorocformamidine, which also is suspected to be present only in one (syn) configuration.

The third component in the mixture was identified as 1-carboethoxyperfluoroguanidine (C_2 PFG), $NF_2C(=NF)NFCO_2C_2H_5$, by comparing its fluorine NMR spectrum with that of an authentic sample.

Following mechanism is proposed to explain the results of the above fluorination:



It appears that trifluoro derivative of 1-carboethoxy-3-cyanoguanidine, postulated intermediate in this reaction, on further fluorination undergoes two competing reactions: (1) displacement of CN^- by fluorine to give C_2 PFG, or (2) displacement of $-\text{NFCN}$ group to give $\text{FC}(=\text{NF})\text{NFCO}_2\text{Et}$. The reaction of the latter with fluorine would account for the formation of $\text{NF}_2\text{CF}_2\text{NFCO}_2\text{Et}$.

3. Experimental: Fluorination of 1-Carboethoxy-3-cyanoguanidine

1-Carboethoxy-3-cyanoguanidine was synthesized in the reaction between cyanoguanidine and ethyl chloroformate, following a known procedure.*

* D. W. Kaiser and J. T. Thurston, J. Org. Chem., 17, 186 (1952).

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II Technical Discussion, B (cont.)

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A solution (mainly suspension) of 31.2 g (0.2 mole) of 1-carboethoxy-3-cyanoguanidine in 350 ml of acetonitrile was fluorinated at 0 to -10°C until ca. 1.2 moles of fluorine was consumed. The resulting pale-yellow solution was washed with 1,700 ml of ice water and phases were separate. The organic phase was then washed with 1,200 ml of ice water and the water-insoluble liquid amounted to 30 grams. The material was dissolved in 300 g of methylene chloride. The solution was dried and filtered. A 30% aliquot of the methylene chloride solution was worked up to give 5.5 g of a pale-yellow liquid, b.p. $40-60^{\circ}\text{C}/25\text{ mm.}$ The product was found to be a mixture containing three components and individual compounds were separated by gas chromatography. The lowest boiling component was identified as ethyl N-fluoro-N-(difluorodifluoramino)methylcarbamate.

Anal. Calc'd for $\text{C}_4\text{H}_5\text{N}_2\text{F}_5\text{O}_2$: C, 23.08; H, 2.42; N, 13.46; F, 45.65

Found: C, 23.4; H, 2.7; N, 13.6; F, 43.2.

Its infrared spectrum (Figure 3) is consistent with the structure.

The 60-mc proton NMR spectrum of the compound showed only C_2H_5 group.

The 56.4-mc fluorine NMR spectrum (Figure 4) was obtained in carbon tetrachloride solution with CFCl_3 added as internal reference. The spectrum exhibits three signals. The broadened signal at -19.8 ppm is in the region of NF_2 group bonded to a saturated carbon atom. The broadened signal at $+77.4\text{ ppm}$ is assigned to $-\text{NFCO}-$ fluorine. The doublet at $+97.9\text{ ppm}$ ($j \sim 12\text{ cps}$) is assigned to $-\text{CF}_2-$ fluorines. The origin of the 12-cps splitting in the up-field doublet was uncovered by a spin decoupling experiment (see insert, Figure 4). In the expanded spectrum, the signal at $+77.4\text{ ppm}$ showed an unresolved triplet character. When the sample was irradiated at the $-\text{NF}_2$ frequency, the signal at $+77.4\text{ ppm}$ occurred as a well resolved triplet. An expanded spectrum of this triplet and the up-field doublet showed that the splittings of each pattern are the same. This indicates that $-\text{NFCO}-$ is coupled to $-\text{CF}_2-$ fluorines with a 12-cps splitting. It is also slightly coupled to NF_2 which obscured the triplet pattern.

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II Technical Discussion, B (cont.)

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The other compound, present in the mixture in highest concentration was identified as ethyl N-fluoro-N-(fluorofluorimino)methylcarbamate.

Anal. Calc'd for $C_4H_5N_2F_3O_2$: C, 28.24; H, 2.96; N, 16.47; F, 33.51.

Found: C, 28.4; H, 3.0; N, 16.9; F, 33.6

Its infrared spectrum (Figure 5) is consistent with the structure.

The 60-mc proton NMR spectrum of the compound showed the presence of $-C_2H_5$ group only.

Its 56.4-mc fluorine NMR spectrum (Figure 6) was obtained in carbon tetrachloride solution with $CFCl_3$ added as internal reference. The assignments are as follows. A broad signal at +15.0 ppm is assigned to the fluorimino fluorine $\underline{NF} = \underline{CF}$ -; the doublet at +53.2 ppm is assigned to the $-NFCO-$ fluorine ($j \sim 26$ cps), and the doublet of doublets at +63.4 ppm is assigned to $-\underline{CF}-$ fluorine. The splitting patterns are assigned as follows: the fluorimino fluorine experiences a small coupling (13 cps) to the $-\underline{CF}-$ fluorine. This splitting is apparently obscured by nitrogen quadrupole broadening. If the $-\underline{CF}-$ quartet is observed while irradiating at the fluorimino frequency, the quartet collapses to a doublet. This proves the 13 cps coupling. The $\underline{NFCO}-$ fluorine is split into a doublet by $-\underline{CF}-$ fluorine with a $j \sim 26$ cps. This is verified by observing the $-\underline{NFCO}-$ resonance while irradiating at the $-\underline{CF}-$ frequency. The doublet collapses to a singlet (see insert, Figure 6). Moreover, the quartet collapses to a doublet if the $-\underline{NFCO}-$ is irradiated.

The NMR data indicates the occurrence of only one isomer, and from the magnitude of $-\underline{CF}-$ to $-\underline{NFCO}-$ coupling it appears that syn isomer is present.

The third component present in the mixture was identified as 1-carboethoxyperfluoroguanidine, C_2PFG ; its fluorine NMR spectrum was found to be identical with that reported* for C_2PFG .

* Aerojet Report No. 0235-01-23 (Quarterly), August 1965, Figure 12 (Confidential).

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II Technical Discussion (cont.)

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

1. Introduction

Fluoroammonium perchlorate, SAP, was previously synthesized and characterized.* The objective of further work in this area was to synthesize larger quantities of the salt required for determination of its physical and chemical properties. Therefore, the work of the past year was concerned with further improvements in the synthesis and with the development of acceptable purification techniques.

2. Discussion

Based on preliminary original findings, it appeared that SAP is a relatively stable salt and that larger amounts of the material could be synthesized and stored. The work of the past year showed that this was the case; batches of 5 to 10 g of the salt were prepared on a routine basis.

The experimental procedure adopted for SAP's synthesis consisted of warming a solution of isopropyl N-fluorocarbamate in an excess of 70 to 72% perchloric acid until the evolution of carbon dioxide ceased. The resulting solution was then concentrated at reduced pressure to remove the excess of perchloric acid; SAP remained as a solid. The crude material was then dissolved in ethyl acetate and precipitated by the addition of chloroform. The material purified in this manner still contains 1 to 3% of a foreign material, tentatively identified as isopropylidinedimmonium perchlorate.** Attempts to vary the reaction conditions failed to suppress the formation of this contaminant. Similarly, a variation of crystallization conditions also did not improve product purity. Subsequently, it was found that SAP of high purity can be obtained by sublimation (60°C/0.05 mm) of the crystallized SAP. The contaminant, apparently is less volatile than SAP and remains as a residue. Sublimation, however, did not appear attractive for large-scale purification of the salt. Subsequently, it was found that the material could be purified by liquid chromatography on a silica gel column in ethyl acetate solution.

* Aerojet Report No. 2945 (Summary), October 1964, p. 34 (Confidential).

** Aerojet Report No. 0235-01-22 (Quarterly), May 1965, p. 15 (Confidential).

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II Technical Discussion, C (cont.)

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When the salt became readily available in gram quantities, a more thorough investigation of its properties was resumed. Fluoroammonium perchlorate is a white solid melting at 105°C with decomposition. It is very sensitive to moisture and must be handled in a dry atmosphere at all times. The material can be kept for several hours at room temperature in glass containers but decomposes on prolonged storage. At -20°C , SAP is stable in glass for at least 1 month. In nickel containers, SAP is storable for several months at room temperature, whereas in Monel, stainless steel, or Teflon containers, a marked decrease in stability is shown.* Differential thermal analysis of SAP showed a sharp exotherm at 105°C . This is the same temperature at which fluorammonium methanesulfonate decomposes.

The infrared spectrum of SAP** was obtained by subliming the material on a sodium chloride window. The N-F absorption was apparently obscured by the $+ClO_4$ absorption; both NH-stretch ($3.05\ \mu$) and NH-bend ($7.03\ \mu$) vibrations were shifted by approximately $0.15\ \mu$ to shorter wavelengths as compared with those of ammonium perchlorate.

The impact sensitivity of sublimed SAP was investigated; no firing occurred below 20 cm (2 kg) and the 50% level varied between 25 and 30 cm (50% RDX = 25 cm). The determination of SAP's sensitivity to static electricity (an argon atmosphere) showed 50% firing level of 5 joules, compared with 8 joules for RDX. Because of the relative insensitivity of SAP, manipulations are now conducted without remote handling techniques.

Some simple chemical reactions of fluorammonium cation were investigated. Fluorammonium methanesulfonate (SAM) liberated approximately 50% of theoretical nitrogen in a reaction with water. Both ammonia and hydrazine were found in the aqueous solution but nitrate ion, nitrite ion and hydroxylamine were absent. Isopropyl N-fluorocarbamate reacted with aqueous base to yield isopropyl N-hydroxycarbamate. Therefore, it was expected that hydroxylamine would be produced in a reaction between fluoroammonium salts and alkali. However, this was not the case; inorganic salts only were obtained when SAM was treated with methanolic sodium methoxide.

* Aerojet Report No. 0235-01-23, August 1965, p. 15 (Confidential).

** Aerojet Report No. 0235-01-22, (Quarterly), May 1965, p. 14 (Confidential).

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II Technical Discussion, C (cont.)

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Only a small amount of n-butylhydrazine was produced in the reaction between SAM and n-butylamine.

The reaction of SAM with acetic anhydride gave N-methylacetamide, probably via N-fluoroacetamide intermediate, followed by Hoffman rearrangement and the reaction of the resulting isocyanate.

Some attempts were made to synthesize other fluorammonium salts. Fluoroammonium nitrate would be a useful oxidizer, but the salt was not obtained in the following metathetical reaction. In the first reaction, SAP was treated with silver nitrate in acetonitrile solution resulting in a gradual decomposition. A similar reaction between SAP and sodium nitrate in acetonitrile also resulted in a complete decomposition of SAP.

3. Experimental

a. Reaction of SAP with Silver Nitrate

One g of silver nitrate was added to a solution of 0.5 g of SAP in 10 ml of acetonitrile. Gas evolution began immediately, and oxidizing power toward KI was lost within 2 hours.

b. Reaction of SAP with Sodium Nitrate

One g of sodium nitrate was added to a solution of 0.5 g of SAP in 10 ml of acetonitrile. Decomposition with gas evolution took place at the surface of the sodium nitrate crystals.

III. SUMMARY

A. REACTIONS OF DIFLUORAMINE

The reaction of α,α -dibromo- α -nitrotoluene with difluoramine in fuming sulfuric acid produced α,α -dibromo- α -difluoraminotoluene and α -bromo- α,α -bis(difluoramino)toluene. Attempts to replace the remaining bromine under more forcing conditions were unsuccessful.

Bromopicrin was unreactive toward difluoramine under a variety of reaction conditions. The self-condensation product of dinitroethane, $\text{CH}_3-\underset{\text{NO}_2}{\underset{|}{\text{C}}}=\text{N}-\text{OC}(\text{NO}_2)_2\text{CH}_3$ or $\text{CH}_3-\underset{\text{NO}_2}{\underset{|}{\text{C}}}=\text{N}-\overset{\text{O}}{\underset{|}{\text{C}}}(\text{NO}_2)_2\text{CH}_3$ also did not react with difluoramine.

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III Summary, A (cont.)

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Benzotrichloride reacted with difluoramine in fuming sulfuric acid to give α -difluoramine- α,α -dichlorotoluene, but produced no higher substitution products.

Poly-(1-chloro-1-nitroethylene) did not react with difluoramine in either fuming sulfuric acid or fluosulfonic acid, apparently because of insolubility.

The nitrosation of 1,1-dinitropropane gave 1,1-dinitro-1-nitroso-propane, identified as its Diels-Alders adduct. The reaction of the nitroso compound with difluoramine in fuming sulfuric acid gave 1,1-dinitropropane.

The reactions of α -bromo- α,α -bis(difluoramino)toluene, α,α -dichloro- α -difluoramino-toluene and α,α -dibromo- α -difluoramino-toluene with sodium methoxide gave dimethyl carbonate anil. The latter reactant gave α -bromo- α -fluoriminotoluene with milder bases such as ammonia and nitronate anion.

The reactions of 1-difluoramino-butane and 2-difluoramino-butane with sulfuric acid gave the N-fluoroimmonium ions resulting from migration of the methyl and ethyl group, respectively. Cyclopentyl-difluoramine underwent a similar rearrangement, with ring expansion.

1,2-Bis(difluoramino)cyclohexane reacted with sulfuric acid to give a complex mixture, according to the NMR spectra of the solution. With fluosulfonic acid, however, the imonium ion resulting from ring expansion with migration of the adjacent methylene group was formed. An attempted difluoramine addition to this ion was unsuccessful.

B. DIRECT FLUORINATION

The fluorination of n-butylurea, N-sec-butylcarbamate and methyl α -carbomethoxyaminobutyrate in acetonitrile gave the corresponding alkyl difluoramines in 30-70% yields.

The fluorination of N-3-hydroxypropylformamide gave 3-difluoramino-propyl formate.

The fluorination of ethyl methoxycarbamate gave N,N'-dimethoxy-N,N'-dicarboethoxyhydrazine.

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III Summary, B (cont.)

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1-Carboalkoxyperfluoroguanidines, $\text{NF}_2\text{C}(=\text{NF})\text{NFCO}_2\text{R}$ ($\text{R} = \text{CH}_3$, C_2H_5 , $i\text{-C}_3\text{H}_7$, and $n\text{-C}_4\text{H}_9$) were obtained in 10-15% yields in the fluorination of 1-carboalkoxyguanidines in acetonitrile.

1,3-Dicarboalkoxyperfluoroguanidines, $\text{NF}=\text{C}(\text{NFCO}_2\text{R})_2$, ($\text{R} = \text{C}_2\text{H}_5$ or $i\text{-C}_3\text{H}_7$) were obtained in yields of 40 to 50% by the fluorination of 1,3-dicarboalkoxyguanidines. The corresponding 1-carboalkoxyperfluoroguanidines were also produced in 10-15% yields in these fluorinations.

1,3-Dicarboalkoxyperfluoroguanidines did not react with methanol even at 60 to 65°C, indicating that their $\text{C}=\text{NF}$ bond is less reactive than that of PFG.

1,3-Dicarboisopropoxyperfluoroguanidine underwent decomposition on treatment with aqueous ammonia (25°C) or with anhydrous ammonia (-25°C). Isopropylcarbamate was identified as one of the decomposition products.

An attempt to nitrate 1,3-dicarboisopropoxy-perfluoroguanidine with 100% nitric acid led to decomposition.

The fluorination of 1-carboethoxy-3-cyanoguanidine gave a mixture of NF compounds from which $\text{NF}_2\text{CF}_2\text{NFCO}_2\text{Et}$, $\text{CF}(=\text{NF})\text{NFCO}_2\text{Et}$, and $\text{NF}_2\text{C}(=\text{NF})\text{NFCO}_2\text{Et}$ were isolated and characterized.

C. FLUOROAMMONIUM SALTS

The synthesis of fluoroammonium perchlorate, SAP, by the perchloric acid hydrolysis of isopropyl N-fluorocarbamate was carried out in the 5- to 10-g range. The salt is a white solid, m.p. 105°, which is very hygroscopic. It is stable at room temperature in nickel and gives a DTA exotherm at 105°. Its impact and static sensitivities are comparable to those of RDX.

The reaction of fluoroammonium methanesulfonate (SAM) with water gave nitrogen, ammonia, and hydrazine. Acetic anhydride gave N-methylacetamide.

Attempts to prepare fluoroammonium nitrate were unsuccessful.

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IV. CONCLUSIONS AND RECOMMENDATIONS

A. REACTIONS OF DIFLUORAMINE

Although 1,1-dihalo-1-difluoraminoalkanes and 1-halo-1,1-bis(di-fluoramino)-alkanes are readily prepared by the replacement of halo and nitro groups by difluoramine, the halogens of the latter products are not sufficiently reactive for further displacement by difluoramine.

The nitroso groups of 1,1-dinitro-1-nitrosoalkanes are so electron deficient that the compounds function as nitrosating agents rather than alkylating agents toward difluoramine.

α -Halodifluoramines undergo dehalogenation in the presence of mild bases to give fluorimines, which undergo a Stevens-type rearrangement in the presence of strong bases, such as alkoxide.

Primary, secondary, and tertiary alkyl difluoramines and vicinal bis-difluoramines can undergo rearrangement to fluorimonium ions in the presence of strong acids. This reaction may be a cause of difficulties in applying difluoramine reactions to tetrafluorohydrazine adducts. The demonstrated reversibility of the difluoramination of carbonyl compounds must be taken into account in scale-ups in which it is desired to maximize yields based on difluoramine.

B. DIRECT FLUORINATION

The fluorination of 1-carboalkoxyguanidines and 1,3-dicarboalkoxyguanidines provides a convenient source of the corresponding perfluoroguanidine derivatives. Although preliminary efforts to add alcohols and amines to the fluorimino groups of these materials were unsuccessful, this area merits further investigations, because it could lead to a simple route to products now available only through the use of perfluoroguanidines.

C. FLUOROAMMONIUM SALTS

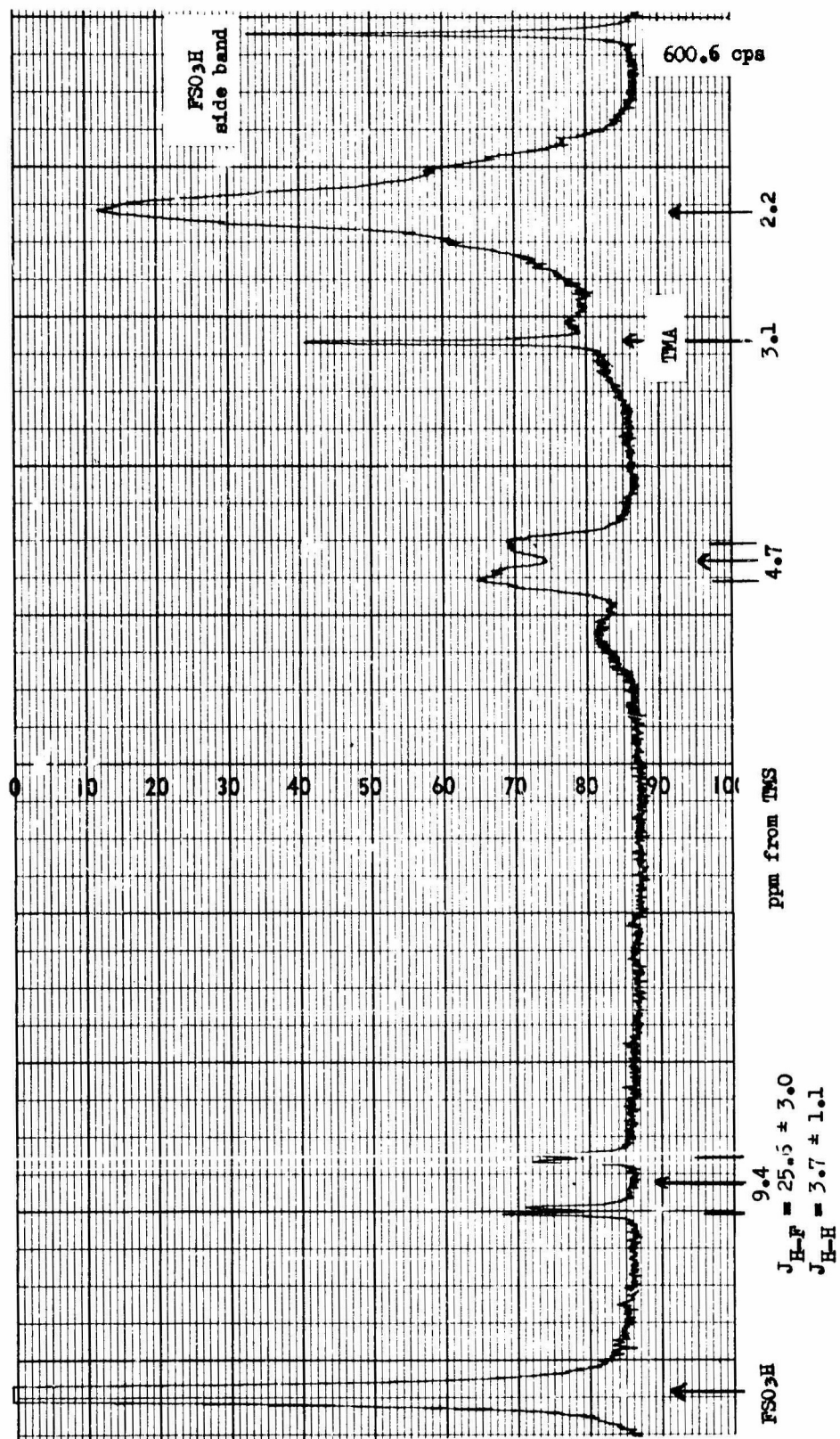
Fluoroammonium perchlorate is a relatively stable inorganic oxidizer and merits further investigation as a propellant ingredient (i.e., thermochemical and ultimately formulation studies).

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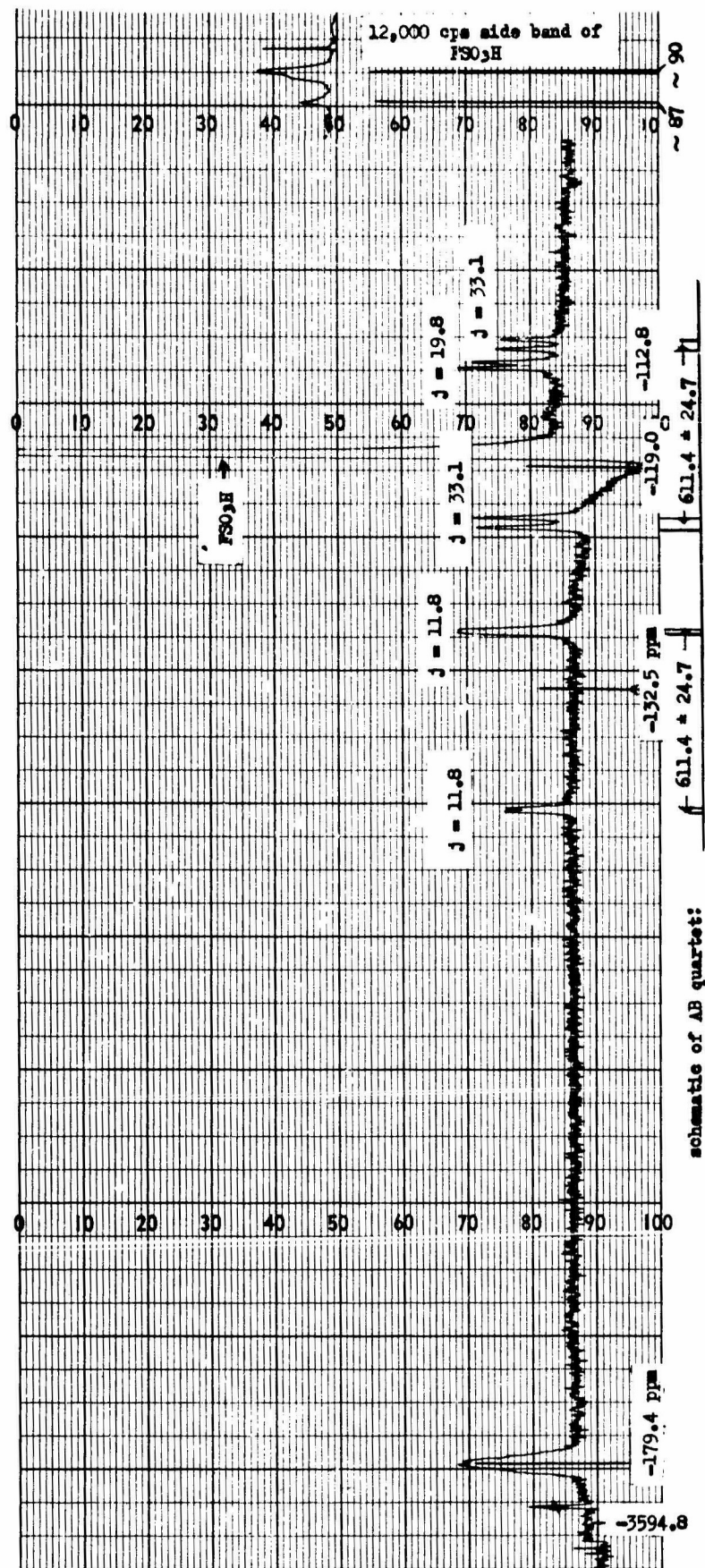
Proton NMR Spectrum of 1,2-bis(difluoraminocyclohexane) Rearrangement Product

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Figure 1

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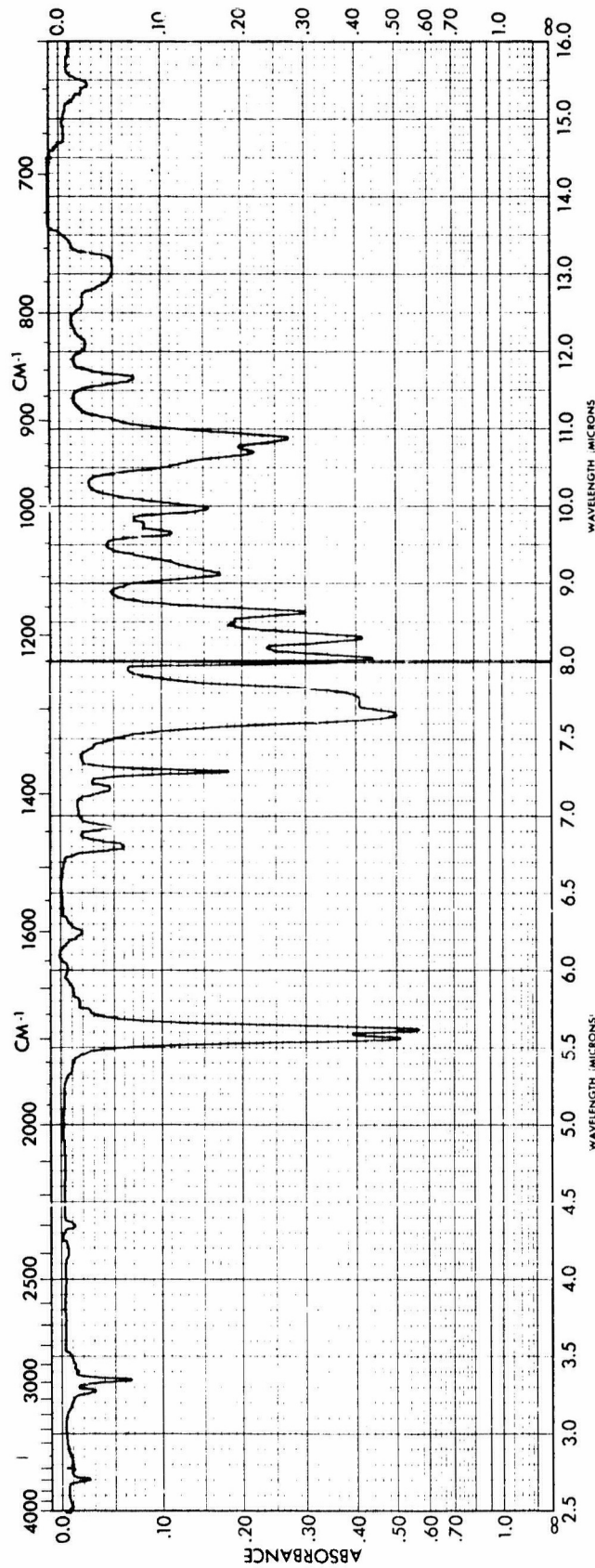
Fluorine NMR Spectrum of 1,2-bis(difluoramino)cyclohexane Rearrangement Product

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Figure 2

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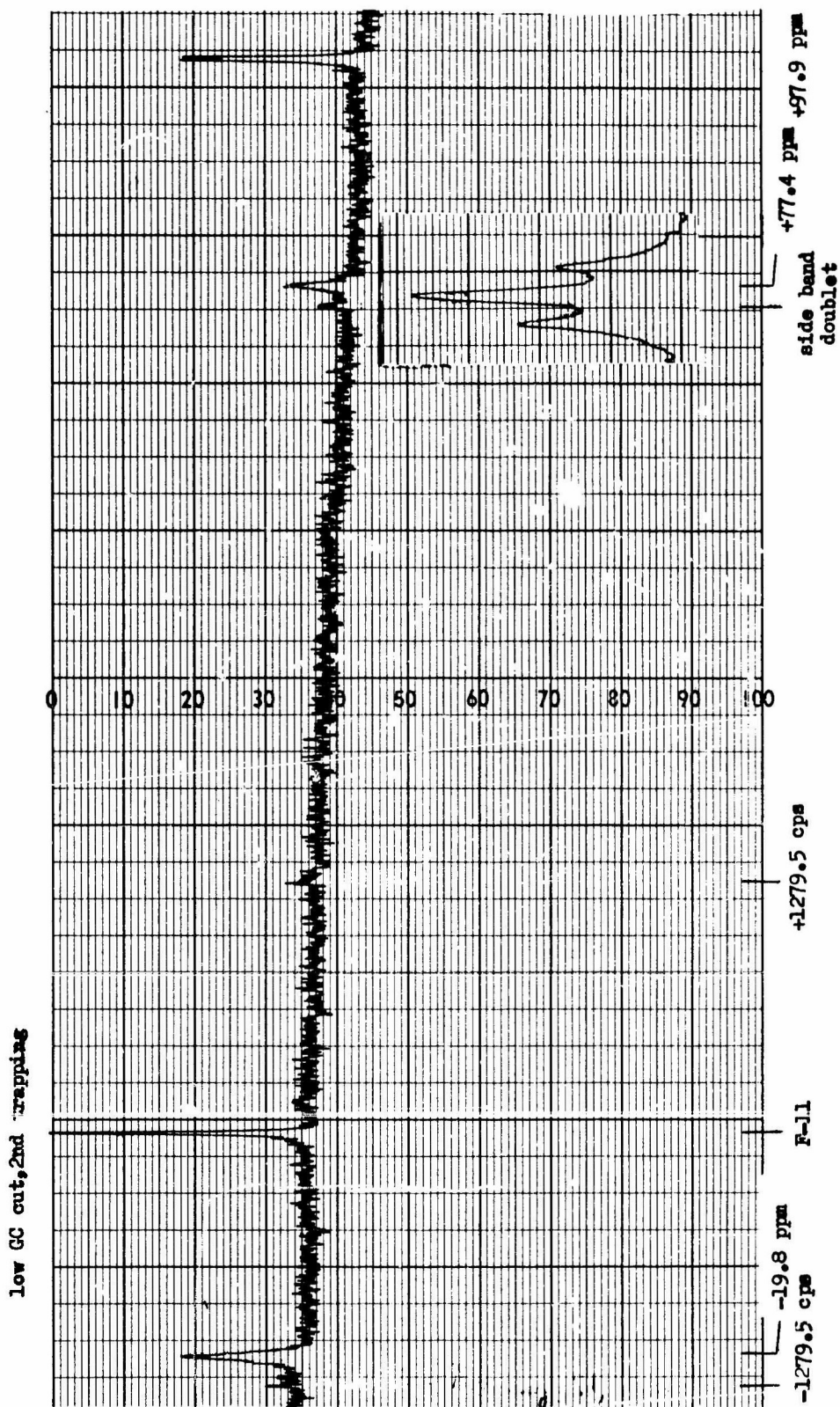
Infrared Spectrum of $\text{NF}_2\text{CF}_2\text{NFCOC}_2\text{H}_5$

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Figure 3

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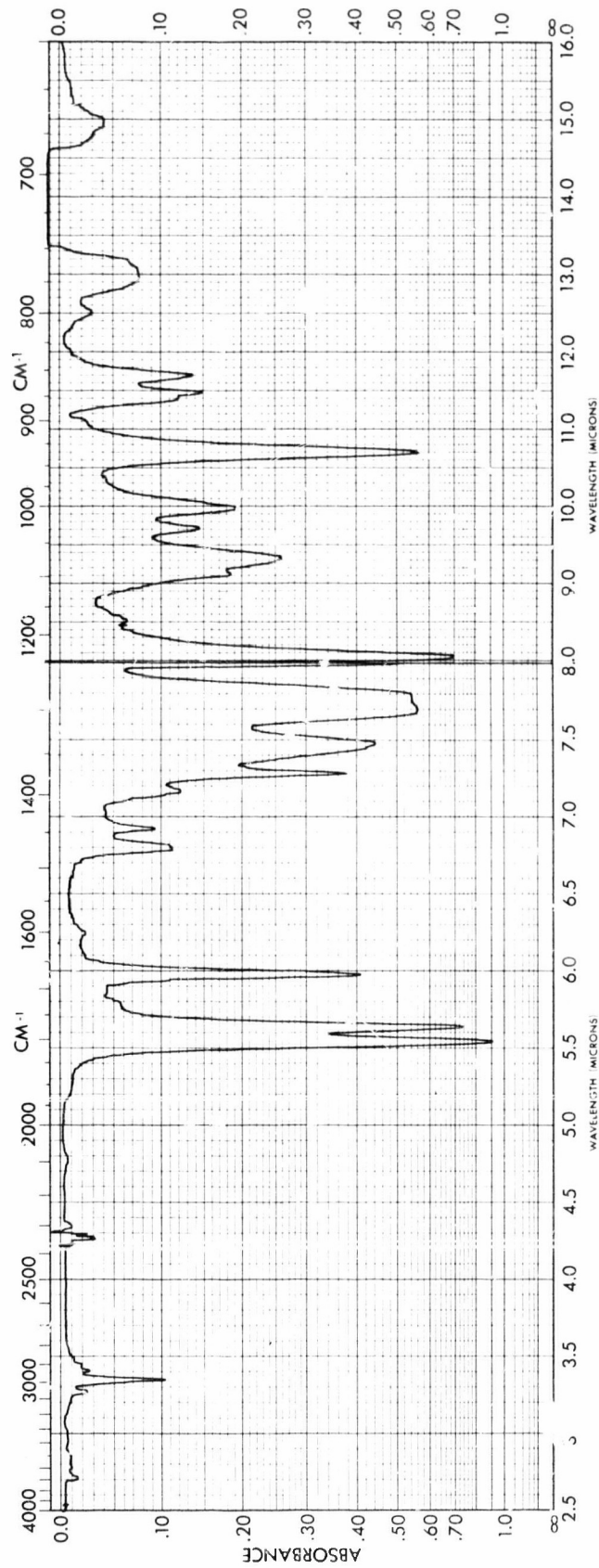
Fluorine NMR Spectrum of $\text{NF}_2\text{CF}_2\text{NFCO}_2\text{C}_2\text{H}_5$

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Figure 4

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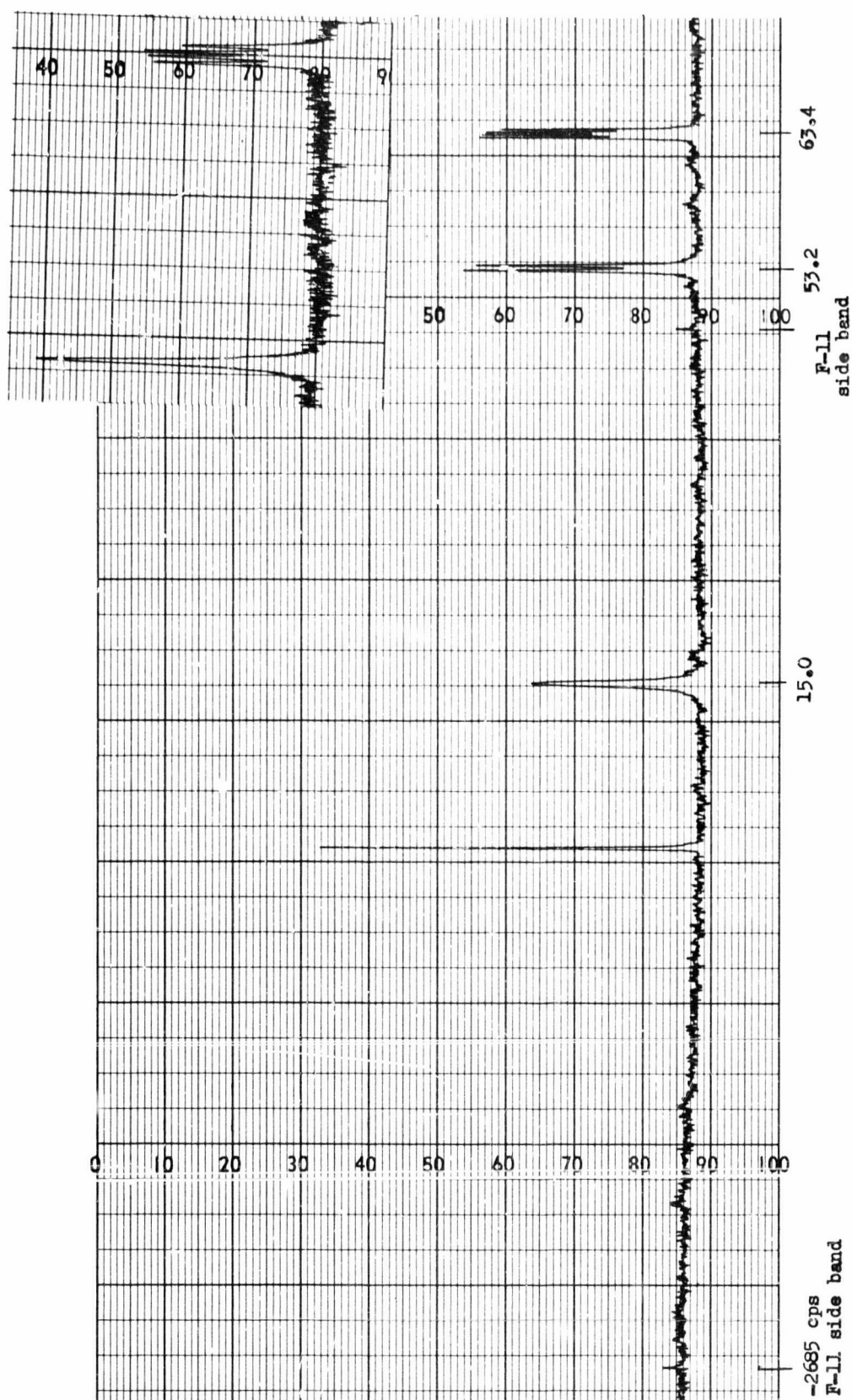
Infrared Spectrum of $\text{NF=CFNFCO}_2\text{C}_2\text{H}_5$

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Figure 5

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Fluorine NMR Spectrum of $\text{NF}=\text{CFNFCO}_2\text{C}_2\text{H}_5$

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Figure 6