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U.S. NAVY
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November 1961
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(Unclassified Title)

RESEARCH IN FLUORO-NITRO COMPOUNDS

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

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Chemical Division

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Aerojet-General

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7 November 1961

Report No. 2099
(Summary)

RESEARCH IN FLUORO-NITRO COMPOUNDS

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

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No. of Pages: 55

Period Covered:

1 September 1960 through 31 August 1961

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AEROJET-GENERAL CORPORATION
Azusa, California

ABSTRACT

The reactions of ketones, aldehydes, and acetylenes with difluoramine in sulfuric acid have produced gem-difluoramines. These are the first widely applicable methods for the preparation of this class of compounds. Other reactions noted with HNF_2-sulfuric acid and some substrates include Michael additions, cyclizations, and nitro replacements.

The fluorination of nitrogenous compounds in aqueous solution has been extended to various amides, ureas, and carbamates. Simple N-fluorination is often accompanied by fluorinative cleavage. The latter course has lead to alkyl difluoramines.

Ethyl N-fluorocarbamate has been obtained from ethyl carbamate. This fluorocarbamate has been converted to a salt which undergoes a number of reactions such as alkylation and halogenation.

A small amount of effort has been devoted to the reaction of anions with tetrafluorohydrazine, attempted preparation of chlorotrifluorohydrazine, preparation of nitro plasticizers and monomers containing the fluorodinitroethyl group, and the preparation of hydrazine salts of nitramines.

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CONTRACT FULFILLMENT STATEMENT

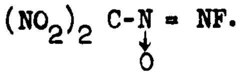
This annual summary report is submitted in partial fulfillment of the contract.

I. INTRODUCTION

This report summarizes the research under Contract Nonr-2655(00), ARPA Order No. 170-61, Project Code 9100, during the period 1 September 1960 through 31 August 1961. The work performed from 1 September 1960 to 31 May 1961 has been reported in Aerojet-General Quarterly Reports Nos. 0235-01-9, 0235-01-10, and 0235-01-11 and will be summarized here. The applicable reports will be listed for each section. Experimental details will be included only for the work of the final quarter. This work is a direct continuation of the research under Contracts Nonr 2655(00) and N7onr 462, Task Order 1, which has been summarized in Aerojet-General Reports No. 1162, 1318, 1509, 1685, and 1877.

During the past year emphasis has been placed upon investigations leading to NF compounds. However, a limited effort has also been devoted to the study of selected nitro compound synthesis. Thus, a few potential monomers and plasticizers have been prepared which contain the fluorodinitroethyl group. The dihydrazine salt of methylenedinitramine was prepared as a potential solid oxidizer in hopes that it would possess properties superior to those of hydrazine nitroformate and hydrazine perchlorate.

Efforts in the NF field have included (1) reactions of anions with tetrafluorohydrazine, (2) attempted preparation of chlorotrifluorohydrazine, (3) reactions of difluoramine, and (4) fluorination in aqueous solution. The first of these was concerned with a limited extension of work described earlier. Reexamination of results reported by Aerojet-General at an earlier time tends to confirm the observations of Esso that products obtained from the salts of gem-dinitro compounds and tetrafluorohydrazine do in fact have the structural feature



$(NO_2)_2\ C\text{-}\underset{\substack{\downarrow \\ O}}{N} = NF.$

Work on the second area of NF effort has not been completed. Thus far, it has not been possible to identify chlorotrifluorohydrazine. However, the route chosen through N_2F_4 and Cl_2NF has given an unstable material which may be the desired product.

Significant accomplishments have been realized in the last two areas. The study of the reactions of difluoramine has proved to be an extremely exciting area of endeavor. For the first time it has become possible to prepare gem-difluoramines in a manner which appears to be a general one. Two types of functional groups have been found which, upon reaction with difluoramine in the presence of concentrated sulfuric acid, yield the desired structures. Although it is still too early to fully evaluate the impact this reaction will have upon the use of NF compounds, it may prove to be as important to development of NF chemistry as oxidative nitration was to nitro chemistry.

Earlier achievements in the last area of investigation were instrumental in developments leading to the successes of the third. Without the impetus of a readily available source of difluoramine through the fluorination of aqueous urea, it is possible that the methods for preparation of the gem-difluoramines may have been overlooked. Important extensions have been made to the aqueous fluorination technique during the past year. Novel fluorinative degradations of substituted ureas and carbamates appear particularly attractive as selective alternate routes to organic difluoramine compounds.

II. TECHNICAL PROGRESS

A. REACTIONS OF DIFLUORAMINE (K. Baum)

1. Discussion

a. Simple Ketones

t-Butyldifluoramine has been prepared by the reaction of difluoramine with either isobutylene or t-butanol in concentrated sulfuric acid.*

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* Quarterly Progress Report on Synthetic Chemistry, Rohm & Haas Report No. P-60-18, 18 November 1960, p. 22 (Confidential).

The rather surprising stability of difluoramine and the adduct in concentrated sulfuric acid suggested the possibility of condensing two moles of difluoramine with carbonyl compounds to prepare gem-difluoramines.

The first example of this reaction was the synthesis of 2,2-bis(difluoramino)propane from acetone and difluoramine in sulfuric acid. Yields of 2,2-bis(difluoramino)propane were generally in the neighborhood of 75%, although in one reaction a 95% yield was obtained. In one case, crystals of the product were formed at the top of the reflux condenser, indicating that an appreciable loss of product was caused by volatility. The reaction has been carried out both by adding acetone to a refluxing mixture of difluoramine and sulfuric acid at room temperature and by adding sulfuric acid to a mixture of difluoramine and acetone. The yield was unaffected by the order of addition. The concentration of the sulfuric acid, however, was critical, and if acid of less than 92% concentration was used, no gem-difluoramine was formed.

The reactions of several other simple ketones with difluoramine in concentrated sulfuric acid were investigated in order to show the generality of the reaction. Cyclopentanone, cyclohexanone, and 3-pentanone gave, respectively, 1,1-bis(difluoramino)cyclopentane, 1,1-bis(difluoramino)cyclohexane, and 3,3-bis(difluoramino)pentane.

A limited investigation was made of other acidic catalysts for this reaction. The reaction of acetone failed in 85% phosphoric acid or 10% sulfuric acid in sulfur dioxide. Cyclohexanone did not give a gem-difluoramine when trifluoroacetic anhydride was used. An attempted reaction of 3-pentanone in methanesulfonic anhydride was also unsuccessful. Fuming sulfuric acid, however, gave more satisfactory results in some cases than did the ordinary concentrated acid.

The difluoramine used in this work was prepared by heating an acidified aqueous solution of difluorourea.* The reactions were carried

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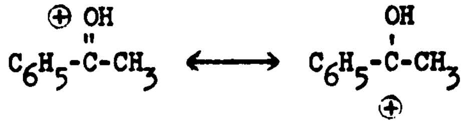
*High-Energy Oxidizer Binders for Solid Propellants, Aerojet-General Report No. 0371-02-2, 15 July 1960 (Confidential).

out at atmospheric pressure, with a nitrogen sweep, and the difluoramine was refluxed in the reaction flask by means of a -80°C condenser. The difluorourea was prepared in 4-mole batches, and could be stored in a refrigerator for 1 to 2 weeks. Storage of frozen aliquots of the urea solution in the generator flasks in a dry ice chest proved more satisfactory, with no detectable decomposition after two months.

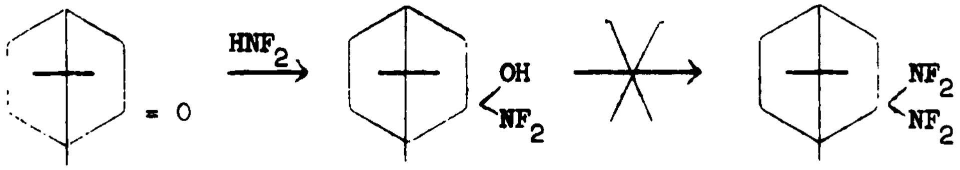
The reaction could not be applied to all classes of ketones. Thus, acetophenone did not form a <u>gem</u>-difluoramine, and starting material was recovered. The failure of this reaction may be due to the high stability of the initially formed cation,



$$C_6H_5\text{-}\overset{\oplus\,OH}{\overset{\|}{C}}\text{-}CH_3 \longleftrightarrow C_6H_5\text{-}\underset{\oplus}{\overset{OH}{\overset{|}{C}}}\text{-}CH_3$$

which is stabilized by the aromatic ring. It has been shown that the reverse of the alkylation reaction can occur if a sufficiently stable carbonium ion can be formed; trityl difluoramine in sulfuric acid formed the trityl carbonium ion and difluoramine.*

The reaction of camphor with difluoramine in sulfuric acid also yielded only unchanged starting material, although there was evidence for the formation of the difluoraminoalcohol in the absence of acid.



The failure of the reaction in acid to proceed to the <u>gem</u>-difluoramine may be caused by the reduced carbonyl carbon-carbon bond angle of the strained system at the carbonyl group. Since this strain is partially relieved in the difluoraminoalcohol, the activation energy in converting this alcohol to the carbonium ion would be greater in this case than in the case of an unstrained ketone.

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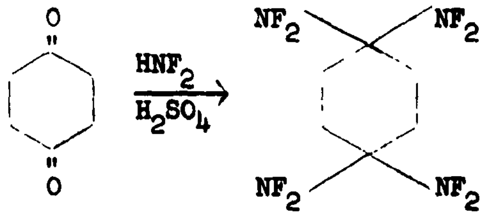
[*] <u>Quarterly Progress Report on Synthetic Chemistry</u>, Rohm & Haas Report No. P-60-18, Pt. II, 18 November 1960, p. 23 (Confidential).

A single experiment was carried out to investigate the feasibility of using gem-difluoramines as storable monopropellants. Thus, 2,2-bis(difluoramino)propane was recovered from its solution in 100% nitric acid after 3 hr at ambient temperature. This area merits further investigation.

b. Diketones

The reaction was next extended to diketones. Several attempts were made using 1,4-cyclohexanedione, as the starting material.



The reaction proceeded erratically when sulfuric acid was added to a refluxing mixture of the dione and difluoramine. Charring occurred, and starting material, as well as material containing hydroxy and NF groups, was recovered. The desired reaction proceeded smoothly, however, when the dione was first dissolved in concentrated sulfuric acid and the difluoramine was then introduced and allowed to reflux for 4-1/2 hr. The tetrakis(difluoramino)cyclohexane, which was obtained in high yield, melted at 103°C, with a phase change at 80°C. It was purified by sublimation at ambient temperature at about 0.1 mm Hg. This reaction has recently been scaled up on another program.* By using remote operation techniques, 50 g of the product was prepared in one batch in 85% yield.

The reaction of acetonylacetone did not yield tetrakis (difluoramino)hexane, but rather 2,5-bis(difluoramino)-2,5-dimethyltetrahydrofuran. This product could be formed by the intramolecular attack of a carbonium ion on a carbonyl or hydroxyl oxygen by a route such as the following:

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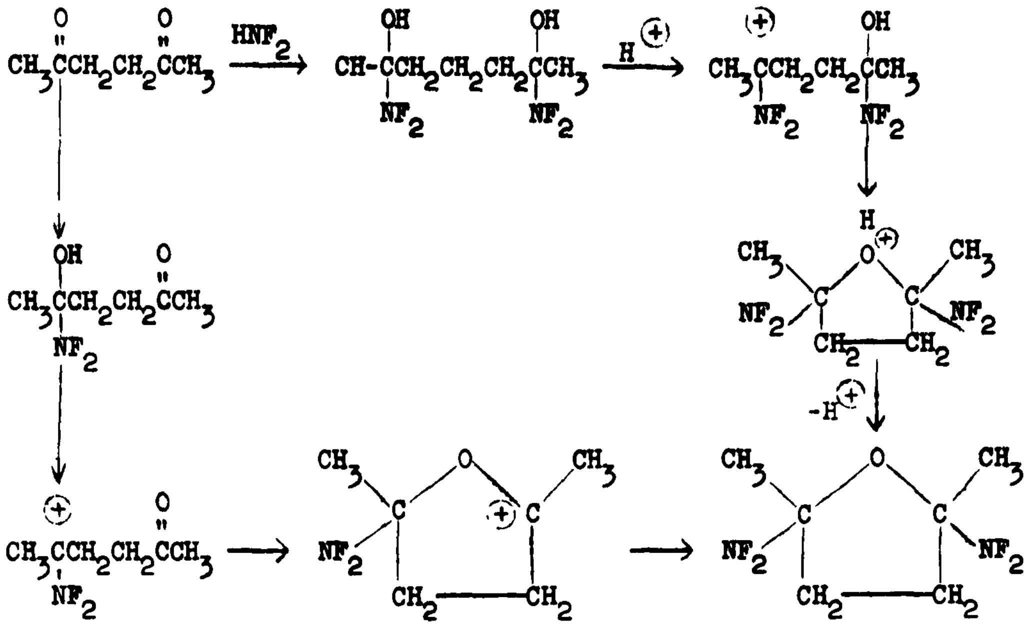
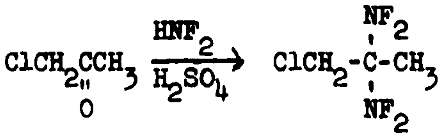
*Contract Nord 18386.



Attempts to react 1,3-pentanedione or 2,3-butanedione with difluoramine in sulfuric acid were unsuccessful.

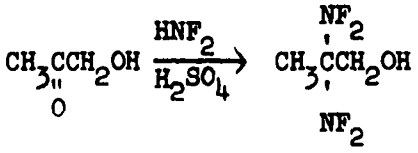
c. Haloketones, hydroxyketones and ketoacids

The effect of various functional groups on the reaction was examined. The reaction of chloroacetone with difluoramine in sulfuric acid proceeded smoothly to give 1-chloro-2,2-bis(difluoramino)propane.



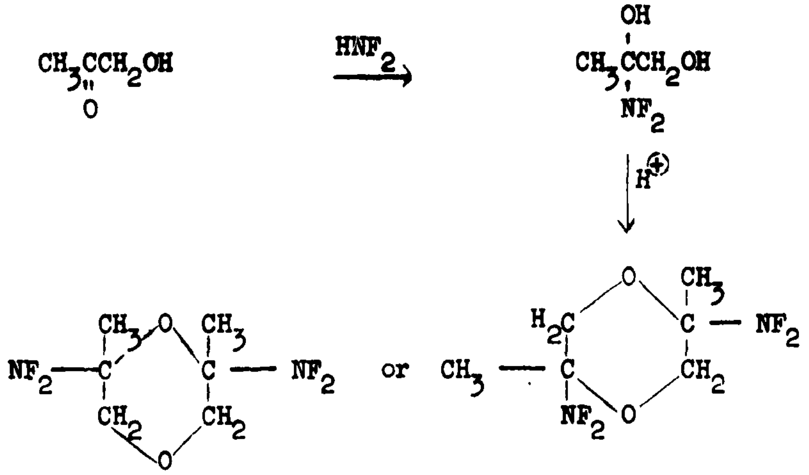
$$\mathrm{ClCH_2\underset{\overset{\|}{O}}{C}CH_3 \xrightarrow[H_2SO_4]{HNF_2} ClCH_2\text{-}\overset{NF_2}{\underset{NF_2}{C}}\text{-}CH_3}$$

It was expected that the reaction of acetol with difluoramine would proceed in a similar manner to form 2,2-bis(difluoramino)propanol.



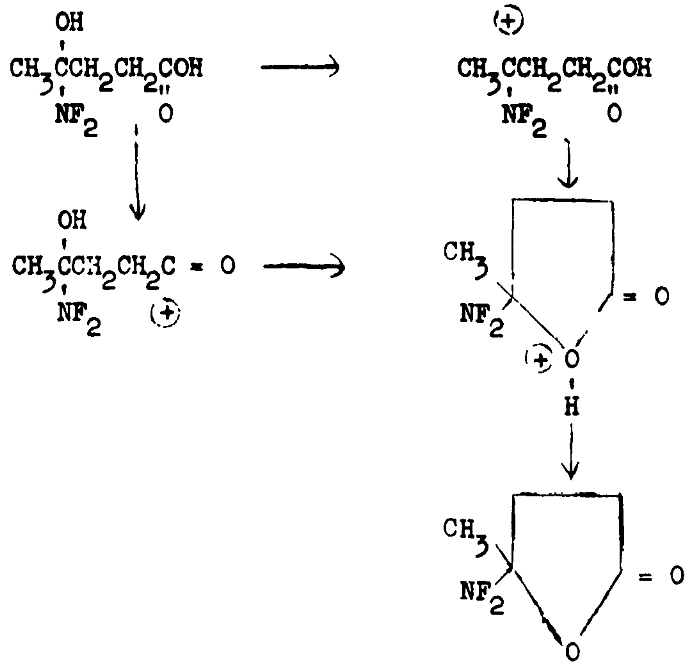
$$\mathrm{CH_3\underset{\overset{\|}{O}}{C}CH_2OH \xrightarrow[H_2SO_4]{HNF_2} CH_3\overset{NF_2}{\underset{NF_2}{C}}CH_2OH}$$

A solid product was obtained (mp 69°) which was sublimed at about 0.1 mm Hg. On the basis of the low volatility and infrared and elemental analysis, the product was identified as a dimeric ether of the initial HNF_2 adduct.



The available data does not allow us to distinguish between these structures.

The first ketoacid which was examined in the difluoramine-sulfuric acid reaction was levulinic acid, which yielded only 4-difluoramino-γ-valerolactone. The intermediate hydroxyacid apparently undergoes esterification through a carbonium or acylium ion.



To determine whether ring formation is a necessary driving force for the esterification of the difluoraminoalcohols in sulfuric acid, the acetone-difluoramine reaction was carried out with the addition of a stoichiometric amount of acetic acid. The gem-difluoramine was formed in this experiment in 95% yield.

The acid-catalyzed reactions of several other ketoacids with difluoramine have been carried out, although analytical data were not obtained because the products presented difficult problems in purification. However, the infrared spectra indicated that NF-containing acids were formed from pyruvic acid, 2-ketoglutaric acid, and 5-ketohexanoic acid.

d. Nitroketones

When polynitroketones were used as starting materials, no reaction took place. Thus, in the reactions of 3-(trinitromethyl)cyclohexanone,[*] 5,5,5-trinitro-2-pentanone,[**] and 5,5-dinitro-2-hexanone,[***] starting material was recovered. Reactions were observed, however, with mononitro ketones. 5-Methyl-5-nitro-2-hexanone[***] underwent a novel denitration reaction to give 2,5,5-trimethyl-2-(difluoramino)tetrahydrofuran. This reaction probably took place by the protonation of the nitro group followed by the loss of nitrous acid.

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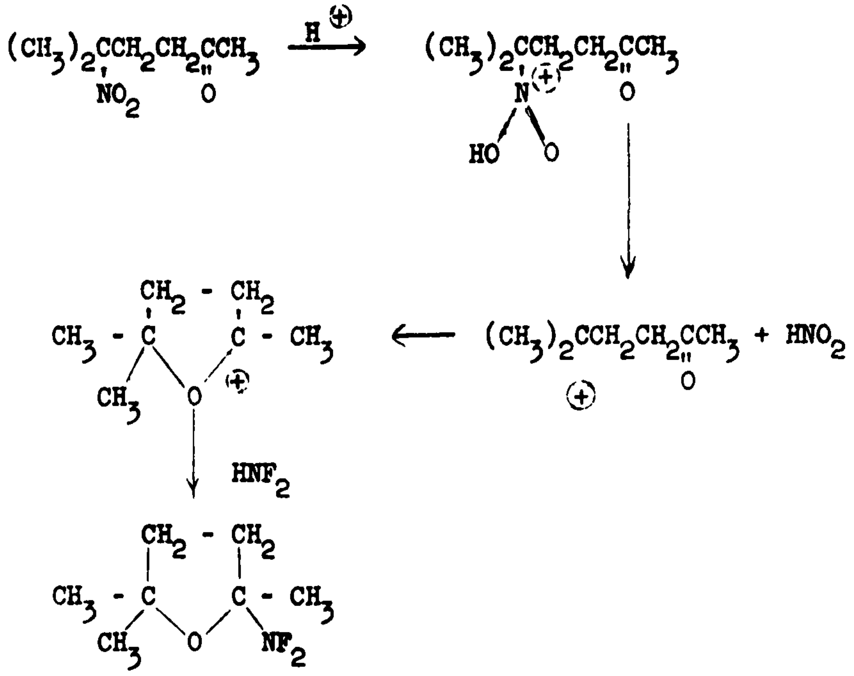
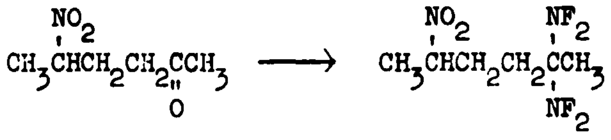
[*] Research in Nitropolymers and Their Application to Solid Smokeless Propellants, Aerojet-General Report No. 590, 27 March 1952, p. 78 (Confidential).

[**] Research in Nitropolymers and Their Application to Solid Smokeless Propellants, Aerojet-General Report No. 563, 31 December 1951, p. 70 (Confidential).

[***] Research in Nitromonomers and Their Application to Solid Smokeless Propellants, Ohio State University, Report No. 1, 15 May 1950, p. 9 (Confidential).



When 5-nitro-2-hexanone* was used as the starting material, this reaction was not observed. The infrared spectrum of the product showed NF_2 and nitro bands, but only a trace of carbonyl. The product, however, decomposed in an attempted purification by gas chromatography. This reaction was repeated, and the product was purified by column chromatography on acid-washed alumina. The elemental analysis and infrared spectrum (Figure 1) showed that the compound was 5-nitro-2,2-bis(difluoramino)hexane.



$$CH_3\overset{NO_2}{C}HCH_2CH_2\underset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3\overset{NO_2}{C}HCH_2CH_2\underset{NF_2}{\overset{NF_2}{C}}CH_3$$

This is the first example of a *gem*-difluoramine with an oxygen-containing functional group. Since this compound is soluble in sulfuric acid, it is apparent that insolubility of the *gem*-difluoramines in sulfuric acid is not a necessary driving force for the reaction.

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*H. Schechter, *J. Am. Chem. Soc.*, 74, 3664 (1952).

The active hydrogen adjacent to the nitro group provides a handle for possible further reactions, such as ketone formation by the Nef reaction or formylation.

In connection with the reaction of 5-methyl-5-nitro-2-hexanone to form 2,5,5-trimethyl-2(difluoramino)tetrahydrofuran, it was of interest to determine whether tertiary nitro groups can generally be replaced by difluoramino groups under these conditions. Thus, t-nitrobutane was treated with difluoramine in sulfuric acid. No insoluble liquid, indicative of t-butyldifluoramine, was formed, however, and quenching the solution yielded acetone and its HNF_2 adduct. In order to ascertain whether t-butyldifluoramine was an intermediate in this reaction, the preparation of this compound from t-butanol was repeated. Although it separated quickly as an insoluble layer and could be isolated by vacuum transfer, on prolonged standing, the product dissolved again in the acid. A similar observation was made previously by workers at Rohm and Haas.* Quenching the acid, however, yielded the same products that were obtained from t-nitrobutane. This reaction may take place by the sulfonation of t-butyldifluoramine or isobutylene to give methanesulfonic acid and an acetone derivative.

e. Olefins and Olefinic Ketones

Isoprene also underwent cleavage under these conditions to yield 2,2-bis(difluoramino)propane. Although this reaction may follow the above course, an alternate mechanism is available involving the reverse of olefin alkylation.

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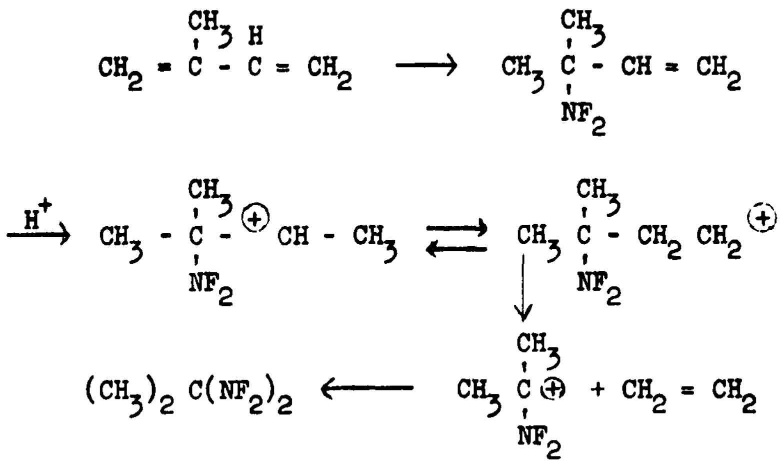
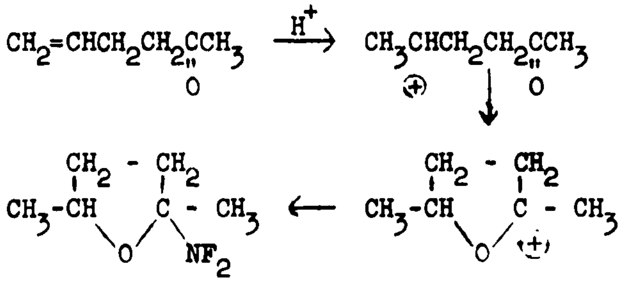
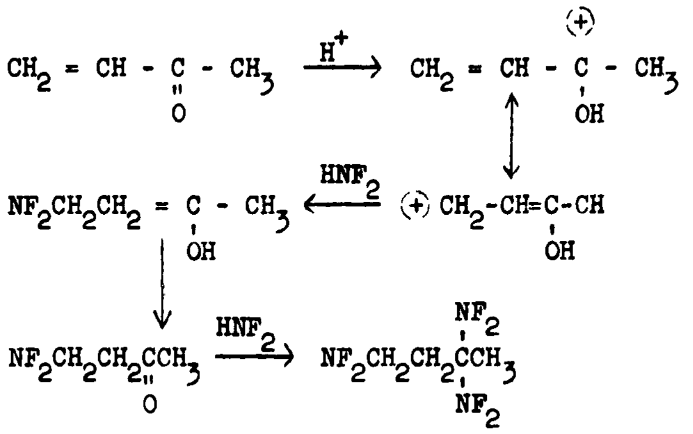
*Dr. William H. Graham, Private Communication, December 1960.



Olefinic gem-difluoramines have not yet been prepared from unsaturated ketones. When 5-hexene-2-one was used as the starting material, 2,5-dimethyl-2-(difluoramino)tetrahydrofuran was formed. The reaction apparently proceeds by protonation of the olefin, followed by cyclization and attack by difluoramine:

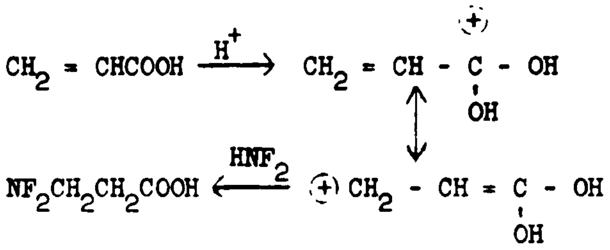


The reaction of methyl vinyl ketone with difluoramine in sulfuric acid has yielded tris(difluoramino)butane. When an insufficient amount of difluoramine was used, however, a product was formed which retained the infrared carbonyl band of the starting material but lost the olefin band. Thus, the first step appears to be an acid-catalyzed Michael addition followed by the replacement of the carbonyl.



The initially formed carbonium ion would react with difluoramine to give predominately the terminally substituted product, since addition to the carbon containing the hydroxyl group should be rapidly reversible.

This mode of addition was confirmed for the acid-catalyzed addition of difluoramine to acrylic acid to give β-(difluoramino)propionic acid.

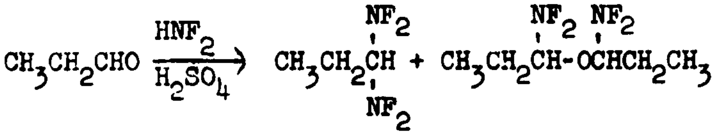


An attempt to extend this reaction to acrylonitrile was unsuccessful, and starting material was recovered.

The reaction of furans with difluoramine in sulfuric acid was also undertaken as an extension to the addition of difluoramine to unsaturated compounds, 2,5-Dimethylfuran yielded an unknown NF compound in a poorly reproducible reaction. Two attempts to use furan as the starting material resulted in explosions after the addition of the first drop to the mixture of difluoramine and sulfuric acid.

f. Aldehydes

Aldehydes have also been converted to *gem*-difluoramines, although the reactions were more sensitive to conditions than those of ketones. Thus, the reaction of propionaldehyde with difluoramine in concentrated sulfuric acid yielded α,α'-bis-(difluoramino)propyl ether and 1,1-bis(difluoramine)propane with the relative yield of the latter increasing with the amount of acid used. When fuming sulfuric acid was used instead of the 96% reagent, the product consisted almost entirely of the *gem*-difluoramine.



$$CH_3CH_2CHO \xrightarrow[H_2SO_4]{HNF_2} CH_3CH_2\overset{NF_2}{\underset{NF_2}{CH}} + CH_3CH_2\overset{NF_2}{CH}\text{-}O\overset{NF_2}{CH}CH_2CH_3$$

The reaction of trioxane with HNF$_2$ in sulfuric acid has given α,α'-bis(difluoramino)methyl ether rather than bis(difluoramino)methane. The latter compound, however, was formed in high yield when fuming sulfuric acid was used. The infrared spectrum (Figure 2) contained strong infrared peaks at 10.0 and 10.4 μ, which are usually shown by *gem*-difluoramines. This curve is quite different from that of α,α'-bis(difluoramino)methyl ether.[*] A Dumas nitrogen analysis on a sample measured by gas volume indicated two nitrogen atoms per molecule. An explosion occurred while 3 ml of the liquid was being transferred from a trap adjacent to the reactor to a vacuum system through 30 ft of 1/4-in. stainless steel tubing. The glassware in both areas was demolished, showing propagation through the long tubing. Since this sample was not analyzed, no firm conclusion could be made regarding the stability of pure bis(difluoramino)methane. However, caution is obviously indicated for work with this compound.

The reaction of chloral hydrate with difluoramine in concentrated sulfuric acid did not give a product insoluble in the acid. The infrared spectrum of the material that was isolated after water-quenching suggested a mixture of the starting material and the alcohol derived from the addition of difluoramine to the carbonyl.

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[*] *Quarterly Progress Report on Synthetic Chemistry*, Rohm & Haas Report No. P-60-24, Pt. II, 13 February 1961, p. 5 (Confidential).

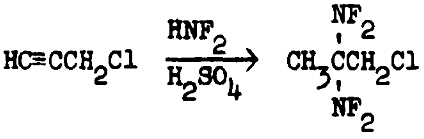
Glyoxal gave a low yield of an NF compound which was not identified.

g. Acetylenes

Another new reaction for the synthesis of NF compounds is the acid-catalyzed addition of difluoramine to acetylenes. This reaction was carried out in the same manner as the reaction of difluoramine with carbonyl compounds in sulfuric acid. Both 1-hexyne and 3-hexyne gave bis(difluoramino)-hexanes, as shown by elemental analysis. The F^{19} NMR spectra* of both adducts (Figures 3 and 4) were single lines, slightly broadened by N^{14} quadrupole coupling, showing that the NF_2 groups are on the same carbon. The proton spectra (Figures 5 and 6) were too complicated for direct assignment because of the molecular asymmetry.

A control experiment was carried out to test the possibility that the addition of HNF_2 to acetylenes proceeds through the hydration of the triple bond to give a ketone. 3-Hexyne was treated with sulfuric acid under approximately the conditions used for the HNF_2 reactions. A 50% yield of 3-hexanone was isolated. Although this result suggests that the HNF_2 addition follows the hydration of the triple bond, the possibility that the direct addition of HNF_2 to the triple bond takes place at a faster rate than hydration cannot be ruled out completely.

The addition of HNF_2 to propargyl chloride has also been accomplished. The product was 1-chloro-2,2-bis(difluoramino)propane, which was identical with the product previously obtained from chloroacetone.



$$HC{\equiv}CCH_2Cl \xrightarrow[H_2SO_4]{HNF_2} CH_3\overset{\displaystyle NF_2}{\underset{\displaystyle NF_2}{C}}CH_2Cl$$

An attempt to carry out a similar reaction with propargyl bromide was unsuccessful, and the starting material was recovered. When methyl propargyl ether was

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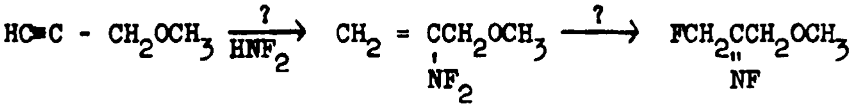
*The NMR analysis was carried out by Dr. D. W. Moore, U.S. Naval Ordnance Test Station, China Lake, California, used as the starting material, a mixture of NF compounds was formed, with infrared absorption in the carbonyl (5.7 μ) and hydroxy (2.9 μ) regions. When this reaction was repeated in the presence of mercuric oxide or with fuming sulfuric acid as the solvent, these peaks were absent and new peaks appeared at 5.9 and 6.0 μ as well as in the NF region. Direct addition of difluoramine to the triple bond might take place under these conditions, with a possible rearrangement of fluorine:



$$HC{\equiv}C-CH_2OCH_3 \xrightarrow[HNF_2]{?} CH_2=\underset{NF_2}{\underset{|}{C}}CH_2OCH_3 \xrightarrow{?} FCH_2\underset{NF}{\underset{\|}{C}}CH_2OCH_3$$

1,6-Heptadiyne gave a high-boiling product with infrared absorption similar to that of the product of the HgO-catalyzed addition to methyl propargyl ether. Phenylacetylene gave a vigorous evolution of gas when it was added to difluoramine and sulfuric acid. No product was isolated. Propiolic acid underwent partial reaction under the usual conditions but the product was not identified. This work is being continued.

Improved analytical data for some of our previously prepared products is given in the experimental section.

2. Experimental

a. New Analyses of Previously Prepared Compounds

2,2-bis(Difluoramino)propane:

Calc'd for $C_3H_6N_2F_4$: C, 24.6; H, 4.1; N, 19.20
Found: C, 24.3; H, 3.96; N, 19.28

1,1-bis(Difluoramino)propane, purified by gas chromatography:

Calc'd for $C_3H_6N_2F_4$: C, 24.6; H, 4.1; N, 19.20
Found: C, 24.9; H, 4.19; N, 18.90

β-(Difluoramino)propionic acid:

Calc'd for $C_3H_5NF_2O$: C, 28.8; H, 4.0; N, 11.2
Found: C, 28.9; H, 4.28; N, 11.20

1,1-bis(Difluoramino)cyclohexane:

Calc'd for $C_6H_{10}N_2F_4$: C, 38.6; H, 5.4; N, 15.0
Found: C, 38.6; H, 5.58; N, 15.0

b. 5-Nitro-2,2-bis(difluoramino)hexane

Difluoramine generated from 200 ml of difluorourea solution* was refluxed for 7 hr over a solution of 2.0 g (0.0138 mole) of 5-nitro-2-hexanone in 30 ml of concentrated sulfuric acid. The solution was allowed to stand overnight, using the dissolved HNF_2 to complete the reaction.

The acid was poured into 200 ml of ice, and the aqueous mixture was extracted with four 50-ml portions of methylene chloride. The methylene chloride solution was washed with two 25-ml portions of water, dried over sodium sulfate, and stripped using an aspirator and Rinco evaporator. The residue consisted of 1.5 g (47% yield) of crude 5-nitro-2,2-bis(difluoramino)-hexane contaminated by a small amount of carbonyl-containing material. An analytical sample was prepared by chromatographing 1.2 g of the crude material on a 175- x 15-mm column of acid-washed alumina (Bio-Rad AG-4) using methylene chloride as the elutant. Total recovery was almost quantitative, and the product was eluted before the impurity.

Anal. Calc'd for $C_6H_{11}N_3F_4O_2$: C, 30.9; H, 4.72; N, 18.0
Found: C, 31.1; H, 4.72; N, 17.55

c. bis-Difluoraminomethane

Difluoramine generated from 200 ml of difluorourea solution was allowed to reflux over 1.0 g of s-trioxane. Fuming sulfuric acid (15 ml) was added, in drops, and the difluoramine was allowed to reflux over this solution for 4 to 5 hr. During this time, the solution gradually became cloudy and an upper layer separated. This layer was vacuum-transferred (100 mm Hg) to a -80°C trap adjacent to the reactor, and 3 ml of liquid was collected. This material was transferred, in increments, to a vacuum system through 30 ft of overhead 1/4-in. stainless steel tubing. The first fraction was analyzed by vapor-

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*Aerojet-General Report No. 0235-01-10, 14 April 1961, p. 9 (Confidential).

phase chromatography and was found to consist of 95% bis(difluoramino)methane with difluoramine and nitrogen as impurities. A Dumas nitrogen determination on a sample measured by gas volume showed 2 atoms of nitrogen per molecule. When about half of the remaining liquid in the trap had been transferred to the vacuum line, a detonation occurred in both traps where the material was being transferred, as well as in an isolated bulb where the previous fraction was stored.

d. Reaction of Isoprene with Difluoramine

Difluoramine generated from 200 ml of difluorourea solution was refluxed over 15 ml of concentrated sulfuric acid. Isoprene (1.7 g) was added, in drops, while the solution was cooled with dry ice in order to keep the temperature at -15 to 0°C. After 4 hr, the excess difluoramine was removed and the product was vacuum-transferred into a -80° trap to yield 0.4 g of 2,2-bis(difluoramino)propane, identified by its infrared spectrum.

B. AQUEOUS FLUORINATION[*] (V. Grakauskas)

1. Discussion

a. Introduction

The feasibility of the fluorination of nitrogenous organic compounds in aqueous solution has been demonstrated, and valuable intermediates, such as N,N-difluorourea and ethyl N-fluorocarbamate, have been prepared[**]. The present study is aimed at extending the scope of this reaction to various nitrogenous systems.

b. Fluorination of Ureas

(1) Alkylureas

It was previously reported[***] that aqueous methylurea undergoes smooth fluorination to give methyldifluoramine and N,N-difluoro-N'-methylurea in approximately equal amounts:

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[*] Aerojet-General Reports No. 0235-01-9, 13 January 1961; No. 0235-01-10, 14 April 1961; No. 0235-01-11, 14 July 1961 (Confidential).

[**] High-Energy Oxidizer Binders for Solid Propellants, Aerojet-General Report No. 0371-02-2, 15 July 1960 (Confidential)

[***] High-Energy Oxidizer Binders for Solid Propellants, Aerojet-General Final Report No. 1960 on Contract AF 49(638)-838, February 1961 (Confidential).

$$CH_3NHCONH_2 + F_2 \xrightarrow{(H_2O)} CH_3NF_2 + CH_3NHCONF_2$$

The fluorination of aqueous ethylurea proceeded similarly to give ethyldifluoramine and N,N-difluoro-N'-ethylurea. Ethyldifluoramine has been reported previously by other investigators,* but the compound has not been completely characterized. A sample of the material was therefore reduced with aqueous potassium iodide to give ethylamine.

The fact that alkylureas undergo fluorination in aqueous solution to yield a mixture of the corresponding alkyldifluoramines and N-alkyl-N',N'-difluoroureas, suggested that allyldifluoramine could possibly be prepared by fluorinating aqueous allylurea. This reaction has yielded a colorless high-boiling liquid and a white solid, possessing strong oxidizing properties. The liquid product was tentatively identified as N,N-difluoro-N'-(2,3-difluoropropyl)-urea on the basis of its elemental analysis and infrared spectrum. The solid, which was insoluble in water and common organic solvents may be a polyallyldifluoramine.

N-Acetyl-N'-methylurea reacted readily with fluorine in aqueous solution to give methyldifluoramine in good yields.

A new method for the preparation of alkyldifluoramines has been found to be the direct aqueous fluorination of N,N'-dialkylureas. Thus, N,N'-dimethylurea gave a high yield of N,N-difluoromethylamine, which was identified by its infrared spectrum.** A small amount of a colorless oxidizing liquid which was isolated from the aqueous fluorination mixture appears, on the basis of the infrared spectrum and an elemental analysis, to be a mixture of N,N'-dimethyl-N-fluorourea and N,N'-dimethyl-N,N'-difluorourea. The reaction apparently proceeds as follows:

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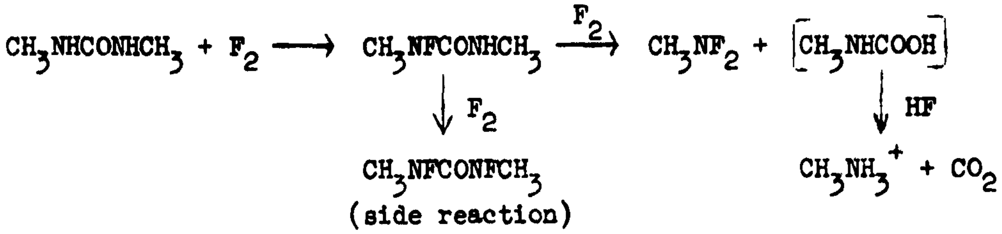
*J. W. Frazer, Paper presented at the Second NF Chemistry Symposium, Pasadena, California, 2-3 December 1959 (Confidential).

**<u>Quarterly Progress Report on Air Force High-Energy Solid Propellant Program</u>, Rohm & Haas Company Report AF-4, May-August 1959 (Confidential).



$$\begin{tikzcd}
CH_3NHCONHCH_3 + F_2 \arrow[r] & CH_3NFCONHCH_3 \arrow[r, "F_2"] \arrow[d, "F_2"] & CH_3NF_2 + \left[CH_3NHCOOH\right] \arrow[d, "HF"] \\
& CH_3NFCONFCH_3 & CH_3NH_3^+ + CO_2
\end{tikzcd}$$

(side reaction)

(2) Arylureas

The fluorination of aqueous phenylurea gave products escaping in gas form during the course of fluorination, as well as products remaining in the aqueous solution. The volatile reaction products which were collected in -80 or -110°C traps amounted to 3 to 4 g per 10 g of phenylurea. This volatile liquid was insoluble in water, possessed strong oxidizing properties, and its density was roughly determined at 1.5 to 1.6 g/cc at -80°C. Gas chromatographic analysis showed that the material contained eight components, four of which were present in amounts of less than 1% each. Of the remaining four components, one was present to the extent of 70%. This major component (bp 24°C) was isolated by fractional distillation. The infrared spectrum of the compound showed three very strong absorption peaks at 9.25, 10.6, and 11.9 μ.

This component was also formed when an aqueous solution of difluorourea, hydrofluoric acid, and benzoquinone was allowed to stand at room temperature. To check the possibility that difluoramine, the hydrolysis product of N,N-difluorourea, was involved, a mixture of benzoquinone and aqueous difluoramine was kept at 20 to 25°C for a period of four days. No volatile reaction products were obtained although this observation, based on one experiment, is not conclusive.

Elemental analysis indicated that the material contained 6 to 8% carbon and 0.2% hydrogen. Several attempts to analyze the compound for nitrogen gave values ranging from 0.4 to 0.9%, which were unexpectedly low. Fluorine analysis by the sodium peroxide method gave values of 12 and 24%, indicating that this method of analysis is not suitable in this case.

One attempt to hydrolyze the compound with aqueous-methanolic potassium hydroxide showed the presence of only 5% fluorine. However, the oxidizing power was still present, indicating that the compound is unusually resistant to the alkaline hydrolysis. The molecular weight by vapor density, extrapolated to zero pressure, was determined to be 129 ±2.

The NMR spectrum[*] showed fluorine, but no hydrogen. The F^{19} magnetic resonance spectrum is a single sharp line. At 56.4 mc, the chemical shift relative to trifluoroacetic acid is -4428 cps. The fact that the line does not show N^{14} quadruple-broadening, as in other NF_2 spectra, would suggest a high degree of molecular symmetry.

Attempts have been made to decompose the compound with either concentrated sulfuric acid or concentrated aqueous sodium hydroxide. In both cases no reaction took place even after prolonged standing at 45 to 55°C.

Although this volatile liquid has not yet been identified, simple, known NF compounds, such as difluoramine, alkyldifluoramines, and fluoroalkyldifluoramines, were eliminated on the basis of either infrared spectra or physical properties. Efforts to identify this compound are being continued.

The aqueous solution of the phenylurea fluorination contained difluorourea, as well as large amounts of tarry materials possessing a strong phenolic odor. The formation of difluorourea involves the cleavage of the C_6H_5-N bond with a displacement of the phenyl group. This type of cleavage was completely unexpected on the basis of experience with the fluorination of the aliphatic urea derivatives, which proceed by cleavage of the carbonyl-nitrogen bond. A sequence to account for the formation of difluorourea is shown below.

$$C_6H_5NHCONH_2 + F_2 \xrightarrow{(H_2O)} C_6H_5NFCONH_2 + HF$$

$$C_6H_5NFCONH_2 + F_2 \xrightarrow{(H_2O)} NF_2CONH_2$$

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[*] Dr. D. W. Moore, U.S. Naval Ordnance Test Station, China Lake, California.

It was found that the direct fluorination of aqueous m- and o-tolylurea proceeded similarly to that of phenylurea. A volatile liquid was produced which was identical to that obtained from phenylurea. The aqueous solution contained N,N-difluorourea. In addition, as was the case with phenylurea, the aqueous reaction mixture contained compounds possessing strong phenolic odor.

(3) Urea

A side reaction in the fluorination of urea has been investigated; the fluorination is run routinely in 4-mole batches. In several cases, the aqueous solution became yellow and turbid during the course of fluorination and deposited small amounts of yellow solid. A similar reaction was also noticed when the incompletely fluorinated aqueous difluorourea solution was allowed to age. The yellow solid was identified as a mixture of biurea and azodicarbonamide. The formation of biurea during the fluorination of urea suggests that monofluorourea, intermediate in the fluorination, reacts with urea to yield the product:

$$NH_2CONHF + NH_2CONH_2 \longrightarrow (NHCONH_2)_2 + HF$$

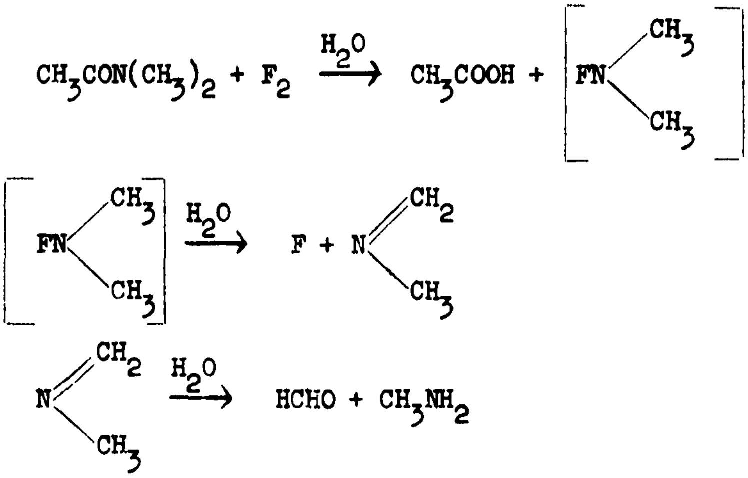
It is not clear why this side reaction occurred in only a few of the runs, although the coupling might be catalyzed by sunlight.

c. Fluorination of Amides

(1) Acetamides

Acetamide was expected to form either N,N-difluoracetamide or its hydrolysis product, difluoramine. Several fluorination attempts have been made, but neither one of the expected products could be produced. Further work with this compound was discontinued. Fluorination of aqueous N-methylacetamide, however, produced methyldifluoramine in high yields.

To obtain additional evidence concerning the mechanism of this reaction, the fluorination of N,N-dimethylacetamide was investigated, and acetic acid and methylamine were identified as products of this reaction. These products may be rationalized by the following series of reactions:



The fluorination product of N,N-dimethylacetamide, N-fluorodimethylamine, would be expected to be unstable and readily eliminate hydrogen fluoride to yield the formaldehyde derivative of methylamine. The acid-catalyzed hydrolysis of this compound would give methylammonium ion and formaldehyde. No attempts were made to identify formaldehyde in this experiment. The first reaction of this sequence appears to be a direct displacement of an acylium ion by fluorine. Hydrolysis of the amide prior to the fluorination and the subsequent fluorination of the resulting amine does not appear probable since earlier attempts to fluorinate alkyl amines or their salts were unsuccessful.

The fluorination of N-methylacetamide could occur in a similar manner as follows:

$$CH_3CONHCH_3 + F_2 \longrightarrow CH_3CONFCH_3 + HF$$

$$CH_3CONFCH_3 + F_2 \longrightarrow CH_3CO^{(+)} + CH_3NF_2 + F^{(-)}$$

$$CH_3CO^{(+)} + H_2O \longrightarrow CH_3COOH + H^+$$

One attempt to fluorinate N-n-butyl-acetamide gave a mixture of NF compounds similar in nature to that obtained on fluorination of N-ethyl-formamide (see below).

Fluorination of aqueous β-acetamidopropionic acid gave β-difluoraminopropionic acid in 40% yield. The material was identified by comparing its physical properties and infrared spectrum with those of the difluoramine adduct of acrylic acid.

The fluorination of acetyl glycine gave products which have not yet been identified.

(2) Formamides

The fluorination of aqueous N-methylformamide was similar to that of N-methylacetamide, giving a high yield of methyldifluoramine:

$$HCONHCH_3 \xrightarrow[H_2O]{F_2} CH_3NF_2$$

It was expected that fluorination of higher N-alkylamides would be analogous to that of N-methylamides, but it was found that this was not the case. Fluorination of the aqueous N-ethylformamide gave a volatile liquid which was found to be a mixture of several NF compounds containing only very small amounts (if any) of the expected ethyldifluoramine. The product of this reaction was tentatively identified, on the basis of infrared spectral evidence, as a mixture of fluoroethyldifluoramines. Additional work is required to establish the structures of these products as well as the number of components.

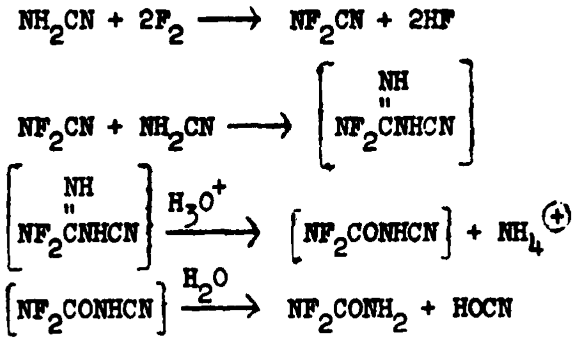
d. Miscellaneous

The fluorination of cyanamide was undertaken with the objective of extending the scope of the fluorination of compounds containing NH_2 groups. This reaction was expected to proceed as follows:

$$NH_2CN + F_2 \xrightarrow{(H_2O)} NHFCN \text{ and/or } NF_2CN + HF$$

Because cyanamide itself dimerizes readily to dicyandiamide or trimerizes to melamine, the fluorinated products were expected to be either monomers, as indicated above, or the corresponding dimers or trimers.

Fluorine was consumed readily by aqueous cyanamide, and nonoxidizing products were deposited. A colorless, low-boiling liquid possessing strong oxidizing properties was also isolated but was not identified. Another product of this reaction was identified as N,N-difluorourea, which was isolated in about 10 to 20% yield. Difluorourea might be produced from urea present as an impurity in the cyanamides, or from cyanamide as follows:



$$\mathrm{NH_2CN + 2F_2 \longrightarrow NF_2CN + 2HF}$$

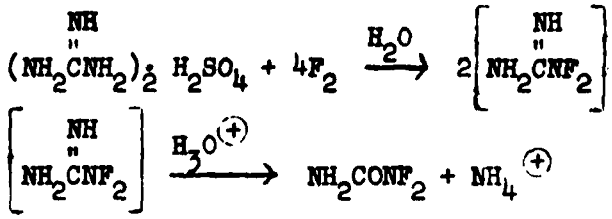
$$\mathrm{NF_2CN + NH_2CN \longrightarrow \left[NF_2\overset{\overset{NH}{\|}}{C}NHCN\right]}$$

$$\mathrm{\left[NF_2\overset{\overset{NH}{\|}}{C}NHCN\right] \xrightarrow{H_3O^+} \left[NF_2CONHCN\right] + NH_4^{\oplus}}$$

$$\mathrm{\left[NF_2CONHCN\right] \xrightarrow{H_2O} NF_2CONH_2 + HOCN}$$

This route would involve the fluorination of cyanamide to the difluoro derivative, which, in turn, would undergo dimerization with unfluorinated cyanamide to yield N,N-difluorodicyanadiamide. This compound might then undergo hydrolysis to the difluorourea.

Aqueous guanidine sulfate was fluorinated with the objective of synthesizing perfluoroguanidine. Fluorine was consumed, but no volatile products were collected in -80 and -110°C traps connected in series with the reaction flask. The aqueous solution yielded N,N-difluorourea in 30% yield. N,N-Difluorourea probably was produced on hydrolysis of the unstable N,N-difluoroguanidine intermediate:



$$\mathrm{(NH_2\overset{\overset{NH}{\|}}{C}NH_2)_2\ H_2SO_4 + 4F_2 \xrightarrow{H_2O} 2\left[NH_2\overset{\overset{NH}{\|}}{C}NF_2\right]}$$

$$\mathrm{\left[NH_2\overset{\overset{NH}{\|}}{C}NF_2\right] \xrightarrow{H_3O^{\oplus}} NH_2CONF_2 + NH_4^{\oplus}}$$

Fluorination of aqueous 1,3-diethyl thiourea produced ethyldifluoramine in low yields. This reaction, except for the yield, is similar to that of symmetrical dialkylureas.

2. Experimental

a. Preparation of β-Difluoraminopropionic Acid

A solution of 26.2 g acetyl β-alanine (0.2 mole) in 350 ml of water was fluorinated with elementary fluorine (diluted with nitrogen: 1:4) at 0 to 5°C until ca. 8 to 10 liters of fluorine gas was passed into the reaction mixture (5 hr). At the end of the run, the aqueous solution was extracted with six 50-ml portions of methylene chloride, followed by six 50-ml portions of diethyl ether. The product was not very soluble in methylene chloride, but extracted readily with diethyl ether. The combined extracts were dried over Drierite, filtered, and the filtrate concentrated. The residue, a pale-yellow liquid, was fractionated and, after removal of some acetic acid, the β-difluoraminopropionic acid was distilled at 46°C/0.1-0.3 mm, n_D^{25} 1.3900. The pure product amounted to 9 g (36% yield). Its infrared spectrum and refractive index were identical with those reported for β-difluoraminopropionic acid.

b. Fluorination of Aqueous Guanidine Sulfate

A solution of 21.6 g guanidine sulfate (0.1 mole) in 350 ml of water was fluorinated at 0 to 5°C with elementary fluorine (diluted with nitrogen 1:4). The reactor was connected in series with -80 and -110°C traps to condense volatile reaction products. The fluorination was continued until 12 liters of fluorine gas was passed into the solution (6 hr). Only a few drops of a colorless liquid accumulated in the -110°C trap during the course of the fluorination. This volatile liquid, possessing strong oxidizing properties, was not identified.

The aqueous solution was extracted with seven 75-ml portions of diethyl ether. On working up the etheral solution, 5 g of N,N-difluorourea was isolated and the material was identified by comparing its infrared spectrum with that of an authentic sample of N,N-difluorourea.

c. Fluorination of 1,3-Diethylthiourea

A solution of 40 g of 1,3-diethylthiourea (0.3 mole) in 650 ml of water (partially in suspension) was fluorinated at 0 to 5°C with elementary fluorine (diluted with nitrogen, 1:4) until 23 liters of fluorine gas was passed into the reaction mixture. During the course of the fluorination, a colorless liquid gradually accummulated in the -80°C trap connected in series with the reactor. At the end of the run, the balance of this low-boiling liquid amounted to 2.5 ml. The crude material was purified by trap-to-trap distillation. The infrared spectrum of this material was practically identical with that of ethyldifluoramine isolated previously on direct fluorination of 1,3-diethylurea.

The infrared spectrum showed the presence of impurities, but no attempts have been made to further purify the crude product.

C. PREPARATION AND REACTIONS OF N-FLUOROCARBAMATES* (V. Grakauskas)

1. Discussion

a. Preparation

The fluorination of aqueous ethyl carbamate gave a mixture of difluoramine and ethyl N-fluorocarbamate.** The NMR spectrum*** of the latter compound is consistent with the assigned structure. The F^{19} resonance is high field from trifluoroacetic acid and the position of the NH compares with that in nitramines.

Failure to isolate the expected N,N-difluorocarbamates from the mixture suggests that compounds with this structural feature are hydrolytically unstable. To test this possibility the fluorination of n-butylcarbamate was carried out in ethylene dichloride to prepare N,N-difluorocarbamate. The expected hydrolytic instability of butyl N,N-difluorocarbamate was confirmed in a reaction with water at 30 to 50°C to yield difluoramine and carbon dioxide:

$$NF_2COOC_4H_9 + H_2O \longrightarrow HNF_2 + CO_2 + C_4H_9OH$$

Alkyl N,N-difluorocarbamates might therefore be used as intermediates for the production of difluoramine. Carbon dioxide-free difluoramine could possibly be obtained by reacting N,N-difluorocarbamates with alcohols.

b. Reactions with Alkalis

It was found that ethyl N-fluorocarbamate could be dissolved in aqueous alkali at 0 to 10°C without decomposition and could be recovered on acidification. This is the first example of a stable NF anion.

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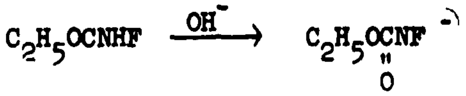
* Research in Fluoro-Nitro Compounds, Aerojet-General Report No. 0235-01-11, 14 July 1961, p. 11 (Confidential).

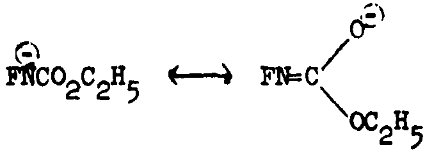
** High Energy Oxidizer Binders for Solid Propellants, Aerojet-General Report No. 0371-02-3, 14 October 1960 (Confidential).

*** Dr. J. P. Freeman, Rohm & Hass Co., see Research in Fluoro-Nitro Compounds, Aerojet-General Report No. 0235-01-11, 14 July 1961 (Confidential).



$$C_2H_5OCNHF \xrightarrow{OH^-} C_2H_5O\underset{\underset{O}{\|}}{C}NF^{(-)}$$

The anion may be considered to be a resonance hybrid in which the negative charge is distributed over the nitrogen and oxygen atoms.



Although aqueous sodium N-fluorocarbamate was relatively stable at low temperatures, it underwent spontaneous decomposition when it was allowed to warm up to 20 to 25°C. The decomposition was highly exothermic, and a water-insoluble colorless liquid separated from the reaction mixture during the course of the reaction. This material has not yet been identified, but its infrared spectrum suggests that the compound is a carbamate. However, it is not hydrazodicarboxylate, azodicarboxylate, iminodicarboxylate, or diethyl oxalate. In addition to the high-boiling liquid, small amounts of carbon dioxide and ethylene were produced. Sodium fluoride, was also isolated.

The first step of the decomposition of the sodium salt of ethyl N-fluoro-carbamate may involve the elimination of fluoride anion with the formation of a nitrene:

$$Na^{(+)}\ {}^{(-)}NFCOOC_2H_5 \xrightarrow[\Delta]{H_2O} :NCOOC_2H_5 + NaF$$

The expected dimerization product of the nitrene, azodicarboxylic acid ester was not found.

Ethyl N-fluorocarbamate decomposed readily with ethanolic sodium hydroxide. One product of this decomposition was identified as iminodicarboxylic acid ethyl ester. A liquid product of this reaction has not yet been identified.

c. Alkylation and Carbethoxylation

The sodium salt of ethyl N-fluorocarbamate reacted at 5 to 10°C with dimethyl sulfate, and the product of this reaction was identified as ethyl N-fluoro-N-methylcarbamate. This compound was also prepared in low yield by direct fluorination of aqueous ethyl N-methylcarbamate:

$$\ominus NFCO_2C_2H_5 \xrightarrow{(CH_3)_2SO_4} CH_3NFCO_2C_2H_5$$

$$CH_3NHCOOC_2H_5 + F_2 \xrightarrow{(H_2O)} CH_3NFCOOC_2H_5$$

The sodium salt of ethyl N-fluorocarbamate also reacted with ethyl chloroformate in aqueous solution to give N-fluorimino dicarboxylic acid diethyl ester in good yields:

$$Na^{+} \, {}^{(-)}NFCOOC_2H_5 + ClCOOC_2H_5 \xrightarrow{(H_2O)} NF(COOC_2H_5)_2$$

d. Halogenation Reactions

The sodium salt of ethyl N-fluorocarbamate reacted with chlorine and bromine to give the corresponding N-chloro and N-bromo derivatives in good yields. N-fluorimino dicarboxylic acid diethyl ester was obtained as a side product.

Both N-chloro-N-fluoro- and N-bromo-N-fluorocarbamates are useful as intermediates for the preparation of NF compounds. Thus, ethyl N-chloro-N-fluorocarbamate reacted instantaneously with sodium hypochlorite to give dichlorofluoramine:

$$ClNFCOOC_2H_5 + NaOCl \longrightarrow Cl_2NF + CO_2$$

Dichlorofluoramine has been previously synthesized by the Allied Chemical Corporation* by reacting sodium azide with chlorine fluoride (ClF). The physical properties and infrared spectrum of the Aerojet-General product agree with those

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*Allied Chemical Corporation, General Chemical Division, Quarterly Progress Report, April-June 1960, Contract No. DA-30-069-ORD-2638 (Confidential).

reported by Allied Chemical. Dichlorofluoramine was also obtained by reacting ethyl N-fluorocarbamate with sodium hypochlorite:

$$HNFCOOC_2H_5 + NaOCl \longrightarrow Cl_2NF + CO_2$$

Diethyl N-fluoriminodicarboxylate also reacted with aqueous sodium hypochlorite to give dichlorofluoramine:

$$NF(COOC_2H_5)_2 + NaOCl \longrightarrow Cl_2NF + CO_2$$

Similar reactions might be used to prepare other nitrogen halides.

Attempts to prepare N-chloro-N-fluoromethylamine by the reactions of ethyl N-fluoro-N-methylcarbamate with aqueous sodium hypochlorite, at 0 to 5°C or at 35°C, were unsuccessful. The starting material was recovered.

$$RNFCOOR' + NaOCl \not\longrightarrow RNFCl + CO_2 + R'OH$$

n-Butyl N,N-difluorocarbamate reacted with aqueous sodium hypochlorite to give chlorodifluoramine:

$$NF_2COOC_4H_9 + NaOCl \longrightarrow ClNF_2 + C_4H_9OCOONa$$

The infrared spectrum indicated a high-purity product, not contaminated by carbon dioxide or tetrafluorohydrazine. This reaction offers a simple route to chlorodifluoramine.

Dibromofluoramine (Br_2NF) and bromochlorofluoramine ($BrNFCl$) are the only two unknown members of the nitrogen trihalide series, exclusive of iodides. The halogenated carbamates have been shown to be suitable intermediates for synthesis of nitrogen trihalides, and attempts were made to synthesize these two compounds.

Since ethyl N-fluorocarbamate reacts with sodium hypochlorite to give dichlorofluoramine, it was expected that the reaction with sodium hypobromite might follow the same course to yield dibromofluoramine. This, however, was not the case and the product of this reaction was mainly difluorodiazine:

$$HNFCOOC_2H_5 + NaOBr \xrightarrow{(H_2O)} N_2F_2$$

The dibromofluoramine was probably an unstable intermediate in this reaction, but decomposed into fluoronitrene and bromine.

Ethyl N-bromo-N-fluorocarbamate was chosen as the intermediate for an attempted preparation of bromochlorofluoramine. When the compound was added to an excess of sodium hypochlorite, a volatile product was obtained which was identified as dichlorofluoramine. It is possible that bromochlorofluoramine was produced in this reaction, but it reacted further with sodium hypochlorite:

$$BrNFCOOC_2H_5 + NaOCl \longrightarrow [BrClNF] \xrightarrow{NaOCl} Cl_2NF$$

When the order of addition was reversed and only a stoichiometric amount of sodium hypochlorite was used, the products were difluorodiazine and elementary bromine. Apparently, in this case, BrClNF decomposed similarly to dibromofluoramine.

From the above experiments it was concluded that both Br_2NF and BrClNF were produced as intermediates, but they underwent further reactions under these reaction conditions. It is also obvious that these nitrogen trihalides are even less stable than Cl_2NF.

e. Attempted Nitration

Attempts to nitrate ethyl N-fluorocarbamate with ethyl nitrate in concentrated sulfuric acid, with the objective of synthesizing ethyl N-fluoro-N-nitrocarbamate, failed to give the desired product. Instead, a vigorous evolution of gaseous products took place which were identified as carbon dioxide and nitrous oxide:

$$NHFCOOC_2H_5 + C_2H_5ONO_2 \xrightarrow{H_2SO_4} N_2O + CO_2$$

f. Reactions with Amines

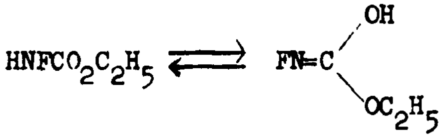
Ethyl N-fluorocarbamate was decomposed in an excess of diethylamine. One product of this reaction was identified as N-carbethoxy-N'N'-diethylhydrazine. Another product, a high-boiling viscous oil, was tentatively identified as the corresponding diethylamide derivative resulting from the reaction of N-carbethoxy-N'N'-diethylhydrazine with excess of diethylamine:

$$NHFCOOC_2H_5 + (C_2H_5)_2NH \longrightarrow (C_2H_5)_2NNHCOOC_2H_5$$

$$(C_2H_5)_2NNHCOOC_2H_5 + (C_2H_5)_2NH \longrightarrow (C_2H_5)_2NNHCON(C_2H_5)_2 + C_2H_5OH$$

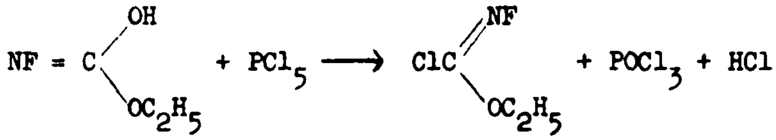
g. Reactions with Phosphorous Pentachloride

Enolization of ethyl N-fluorocarbamate appears possible:



$$HNFCO_2C_2H_5 \rightleftarrows FN{=}C(OH)(OC_2H_5)$$

This possibility suggested that a reaction with phosphorus pentachloride might occur to form the reactive ethyl chloroformate analogue:

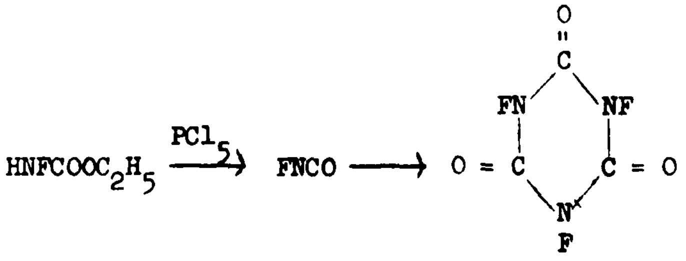


$$NF = C(OH)(OC_2H_5) + PCl_5 \longrightarrow ClC(=NF)(OC_2H_5) + POCl_3 + HCl$$

Substituted carbamates have been reacted with PCl_5 with the formation of the corresponding isocyanates:*

$$RNHCOOR' + PCl_5 \longrightarrow RNCO$$

If the reaction between ethyl N-fluorocarbamate and phosphorus pentachloride would follow this route, N-fluoroisocyanate or its trimer should be produced:



It was found that a mixture of ethyl N-fluorocarbamate and PCl_5 reacts readily at 60 to 80°C to give large amounts of a volatile liquid.

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*H. Wenker, J. Am. Chem. Soc., 58, 2608 (1936).

The product was found to contain several components, but thus far none of them has been identified. The infrared spectrum of the mixture showed the presence of a very strong absorption peak at 4.4 μ, suggesting the presence of the isocyanate group. Another strong absorption peak at 5.5 μ was tentatively assigned to shifted carbonyl. Several strong absorption peaks in the 9 to 12 μ region, together with strong oxidizing properties of the product, suggested the presence of NF. Work is presently in progress to identify reaction products and extend this reaction to other similar NF compounds.

One attempt has been made to react N,N-difluorourea with PCl_5 in an ethylene chloride solution with the objective to synthesize N,N-difluorocyanamide. It was found that on standing overnight at room temperature the mixture evolved a gaseous product which was condensed in a -80°C trap. This material was found to be pure difluoramine. Carbon dioxide was not produced in this reaction.

N,N-Difluorourea also reacted with phosphorus pentoxide at 40°C in an ethylene chloride solution with the formation of difluoramine. Again, high-purity difluoramine not contaminated with carbon dioxide was obtained.

h. Attempted Use as Fluorinating Agents

Several preliminary attempts have been made to explore the uses of ethyl N-fluorocarbamate and N-fluoriminodicarboxylate as fluorinating agents. Attempts to react ethyl N-fluorocarbamate with naphthalene in concentrated sulfuric acid to form 1-fluoro-naphthalene were unsuccessful, and ethyl N-fluorocarbamate was recovered. Ethyl N-fluorocarbamate and acetamide heated at 90 to 95°C did not give N,N-difluoroacetamide; unreacted N-fluorocarbamate was recovered. One unsuccessful attempt was also made to use N-fluoriminodicarboxylate as a fluorinating agent. An equimolar mixture of the material and naphthalene was kept at 90 to 95°C for 7 hr without any apparent reaction.

i. Attempted Preparations of N,N'-Difluorohydrazodicarboxylate and Perfluorotriazinedicarboxylate Esters

Attempts to synthesize diethyl N,N'-difluorohydrazodicarboxylate by reacting the sodium salt of ethyl N-fluorocarbamate with ethyl N-bromo-N-fluorocarbamate led to the formation of diethyl N-fluoriminodicarboxylate:

$$NaNFCOOC_2H_5 + BrNFCOOC_2H_5 \longrightarrow NF(COOC_2H_5)_2$$

Similarly, the N-fluoriminodicarboxylate was produced in the reaction between dichlorofluoramine and the sodium salt of ethyl N-fluorocarbamate:

$$Cl_2NF + 2\ NaNFCOOC_2H_5 \longrightarrow NF(COOC_2H_5)_2$$

In this latter case, the objective was to synthesize diethyl perfluorotriazenedicarboxylate, $NF(NFCOOC_2H_5)_2$.

The results of the latter two experiments suggest that both N,N'-difluorohydrazo- and perfluorotriazenedicarboxylate are unstable reaction intermediates and undergo decomposition in an aqueous medium with the formation of N-fluoriminodicarboxylate. Considerable amounts of carbon dioxide and nitrous oxide (N_2O) were produced in these reactions.

2. Experimental

a. Decomposition of Ethyl N-Fluorocarbamate with Ethanolic Sodium Hydroxide

Over a period of 3 to 5 min, 2.7 g of ethyl N-fluorocarbamate (0.025 mole) was added from a dropping funnel, with stirring at 0 to 5°C, to a suspension of 1.0 g of sodium hydroxide (0.025) in 15 ml of absolute ethanol. An evacuated infrared gas cell was connected in series with the reaction flask to obtain a sample of gaseous products evolved from the reaction mixture.

When all of the N-fluorocarbamate was added, the cooling bath was removed and the mixture was allowed to warm to 20 to 25°C. At this temperature, the sodium hydroxide gradually dissolved and a pale-yellow solution resulted. The reaction was mildly exothermic and cooling was required to keep the mixture at the desired temperature. At the end of 30 min, the mixture was warmed up to 35 to 40°C and kept at this temperature for 10 min to complete the reaction. The infrared spectrum of the gaseous products showed the presence of carbon dioxide and small amounts of ethylene.

The ethanolic solution was concentrated to 5 to 8 ml and the residue was added to 100 ml of cold water. The aqueous mixture was extracted with four 20-ml portions of methylene chloride, the combined extracts were dried and filtered, and the filtrate was concentrated. The residue, ca, 2 ml of a yellow liquid, was fractionated into two fractions:

(1) b.p. 50-55°C/0.1-0.3 mm n_D^{25} 1.4228

(2) b.p. 85-05°C/0.1-0.3 mm n_D^{25} 1.4375

Each fraction amounted to 0.7 to 0.8 g. Fraction (2) partially solidified on standing, and was purified by crystallization from n-pentane to give 0.6 g of white microcrystalline solid, mp 46 to 47°C. This material was identified as iminodicarboxylic acid diethyl ester.*

Analysis: Calc'd for $NH(COOC_2H_5)_2$; $C_6H_{11}NO_4$:

C - 44.71; H - 6.86; N - 8.67.

Found: C - 44.75; H - 6.78; N - 8.76.

b. Decomposition of Ethyl N-Fluorocarbamate with Diethylamine

Five grams of ethyl N-fluorocarbamate was added to vigorously stirred diethylamine (20 ml) at 0 to 5°C. Because the reaction was too vigorous, both components were diluted with methylene chloride (25 ml total) to moderate the reaction. The addition of carbamate was completed in 10 min and the reaction mixture became bright yellow. The cooling bath was removed and the mixture was allowed to warm up to 33 to 35°C. The reaction was exothermic and occasional cooling was required to control the temperature. At the end of 30 min at 33 to 35°C, the reaction was completed. The mixture was allowed to stand at 25 to 30°C for an additional 60 min, and it was then concentrated to remove the solvent and unreacted diethylamine. The viscous residue was diluted with 30 ml of water and the water insoluble oil was extracted with four 20-ml portions of methylene chloride. The combined extracts were dried and filtered, and the filtrate was concentrated. The residual viscous oil was fractionated to give:

(1) 1.5 g colorless liquid, b.p. 70 to 90°C/0.1 to 0.3 mm

(2) 1.0 g orange-yellow liquid, b.p. 110 to 130°C/0.1 to 0.3 mm

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*O. Diels, Ber., 36, 736 (1903).

The material of Fraction (1) solidified partially on standing, and the crude product was purified by recrystallization from n-pentane to give 1g of a white microcrystalline solid, mp 64 to 66°C. The infrared spectrum of this material was found to be very similar with that of N-carbethoxy-N',N'-dimethylhydrazine. An analytical sample (mp 69°C) was obtained on recrystallization from n-pentane.

Analysis: Calc'd for $(C_2H_5)_2NNHCOOC_2H_5$; $C_7H_{16}N_2O_2$:
C - 52.47; H - 10.07; N - 17.48.
Found: C - 52.71; H - 10.0; N - 17.85.

The high-boiling product [Fraction (2)] was redistilled to give a colorless liquid, b.p. 100°C/0.1 to 0.3 mm, n_D^{25} 1.2610, which solidified partially on standing. This material was not identified, but its infrared spectrum is quite similar to that of N-carbethoxy-N',N'-diethylhydrazine.

c. Attempted Preparation of Dibromofluoramine

Three grams of ethyl N-fluorocarbamate was slowly added, with stirring at 0 to 5°C, to a solution of 16 g of bromine (0.1 mole) and 8.0 g of sodium hydroxide (0.2 mole) in 200 ml water. The gaseous products escaping from the reactor did not condense at -80°C. Some of the gaseous material was collected in an evacuated infrared gas cell and submitted for analysis. The infrared spectrum showed that the material was difluorodiazine contaminated with traces of nitrous oxide (N_2O).

d. Attempted Preparation of Bromochlorofluoramine

One gram of ethyl N-bromo-N-fluorocarbamate (0.006 mole) was added in drops, with stirring, to 36 ml of 5.3% aqueous sodium hypochlorite (0.024 mole NaOCl) at 5 to 10°C over a period of 5 min. The reaction occurred instantaneously, with deposition of a yellow liquid which subsequently evaporated. The product was collected in a -80°C trap connected in series with the reactor. At the end of the run this liquid amounted to 0.3 ml. The infrared spectrum of this material showed that it was dichlorofluoramine.

In another experiment, 8.85 g of 5.25% aqueous sodium hypochlorite (0.006 mole NaOCl) was added in drops, with stirring at 0°C, to 1 g

(0.006 mole) of ethyl N-bromo-N-fluorocarbamate over a period of 5 min resulting in a vigorous evolution of gas. The gaseous material was passed through a -80°C trap and collected in an evacuated infrared gas cell. The infrared spectrum showed that the gaseous product was pure difluorodiazine. At the end of the run, the -80°C trap contained some yellow solid which melted on removal of the cooling bath. This material was identified (U.V.) as elementary bromine.

e. Reaction Between Ethyl N-Fluorocarbamate and Phosphorus Pentachloride

A mixture of 6.0 g of ethyl N-fluorocarbamate (0.06 mole) and 21 g of phosphorus pentachloride (0.1 mole) was placed in a 50-ml round-bottomed three-necked flask equipped with a magnetic stirrer, nitrogen inlet tube, and dry ice-acetone reflux condenser. The mixture was warmed up to 70 - 75°C, and an exothermic reaction began which lasted for 5 to 10 min. The reaction product refluxed from the dry ice-acetone condenser. The reaction mixture was kept at 70 to 75°C for 3 hr. During this time, 0.5 ml of a yellow liquid escaped from the reactor and condensed in a -80°C trap connected in series with the reaction flask. The reflux condenser was allowed to warm up to room temperature, and aspirator vacuum was applied to the reaction flask. After 30 min, 9.5 ml of pale-yellow liquid accumulated in the -80°C trap. This fraction was combined with the 0.5 ml of the volatile product obtained previously, and the product was fractionated.

(1)	b.p. 34 to 50°C (pot temp. 50 to 100°C)	1.5 ml
(2)	b.p. 35 to 50°C (pot temp. 120 to 125°C)	1.5 ml
(3)	b.p. 50 to 55°C/20 mm	5 ml
(4)	b.p. 25°C/0.1 to 0.3 mm	2 ml

Products of all fractions were submitted for infrared and gas chromatographic analysis. It was found that Fractions (1) and (2) were similar and contained three components. Fractions (3) and (4) contained 50 to 70% phosphorus oxychloride. Work is in progress to separate and identify all reaction products.

f. Reactions of N,N-Difluorourea with Phosphorus Pentachloride and Phosphorus Pentoxide

Phosphorus pentachloride (8.4 g; 9.04 mole) was placed into a 25-ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, dropping funnel, and a gas-exit tube leading to a -80°C trap. A solution of 3.0 g of N,N-difluorourea (0.031 mole) in 6 ml of ethylene chloride was placed in the dropping funnel and added in drops to PCl_5 at 0 to 5°C, with stirring. No noticeable reaction occurred until the mixture was gradually warmed up to 40°C, at which point a slow gas evolution began and continued for about 45 min. At the end of this period, the -80°C trap contained 2.0 ml of a colorless liquid. The material boiled readily when the cooling bath was removed, and the low-boiling product (1.0 ml) was condensed in another -80°C trap. The low-boiling liquid was identified (infrared spectrum) as pure difluoramine. The high-boiling liquid (1.0 ml) was found to be ethylene chloride.

In another experiment, the mixture of N,N-difluorourea and phosphorus pentachloride in ethylene chloride was allowed to stand at room temperature overnight. Again, difluoramine contaminated only with some ethylene chloride was obtained and condensed in a -80°C trap connected in series with the reactor.

When a solution of 3.0 g of N,N-difluorourea (0.03 mole) in 6.0 ml of ethylene chloride and 6.3 g of phosphorus pentoxide (0.045 mole was warmed up to 40°C and kept at this temperature for 60 min, 1.0 ml of colorless liquid escaped from the reaction flask and condensed in a -80°C trap connected in series with the reactor. This mixture contained 0.7 ml of difluoramine and 0.3 ml of ethylene chloride.

D. REACTION OF DICHLOROFLUORAMINE WITH TETRAFLUOROHYDRAZINE* (P.M. Iloff)

The reaction of dichlorofluoramine with tetrafluorohydrazine was attempted, with the objective of preparing chlorotrifluorohydrazine, a potentially valuable intermediate. A reaction took place readily at 0°C, when dichlorofluoramine was treated with excess tetrafluorohydrazine. The dichlorofluoramine was consumed, and a new material with approximately the same boiling point was

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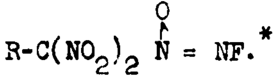
*Aerojet-General Report No. 0235-01-1; 14 July 1961, p. 31 (Confidential).

formed. However, this material decomposed completely after several hours at room temperature, with the formation of chlorine, N_2F_2, and products of attack on glass.

The boiling point, spectral properties, and decomposition products of this material are in line with those expected for chlorotrifluorohydrazine. However, the observed instability indicates considerable difficulty in synthetic applications. Dichlorofluoramine was found to be relatively stable under the conditions in the above reaction.

E. REACTION OF TETRAFLUOROHYDRAZINE WITH ANIONS[*] (K. Baum)

The oxidation of sodium 2-propane nitronate with tetrafluorohydrazine has been reported to give 2,3-dinitro-2,3-dimethyl-butane.[**] In order to avoid this coupling reaction, salts of 1,1-dinitroalkanes were used as starting materials and new NF compounds[***] were obtained. Evidence has since been presented that these compounds are 1-fluoroazoxy-1,1-dinitro-alkanes,  $R\text{-}C(NO_2)_2\overset{\overset{O}{\uparrow}}{N} = NF$.[****] Analytical data obtained at Aerojet-General agree with this assignment.

During the past year, limited additional investigations were carried out in this area. When the reaction of sodium 2-propanenitronate with tetrafluorohydrazine was carried out in the presence of sodium nitrite, some 2,2-dinitropropane was formed, suggesting an intermediate that can be trapped by anions.

An attempt to react the salt of fluorodinitromethane (from the _in situ_ deformylation of 2,2-dinitro-2-fluoroethanol) was unsuccessful. It was shown that the alcohol did not deformylate under these conditions.

The effect of ultraviolet radiation on the reaction of 1,1-dinitrobutane and tetrafluorohydrazine in the absence of solvent was examined. The

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[*] Aerojet-General Report No. 0235-01-9, 13 January 1961, p. 7 (Confidential).

[**] Rohm & Haas Co., Quarterly Report on Synthetic Chemistry, P 58-35, Part II, January 1959 (Confidential).

[***] Aerojet-General Report No. 1877, 13 October 1960, p. 7 (Confidential).

[****] Esso Engineering and Research Corp. Report No. 61-2, June 1961 (Confidential).

reaction was carried out at ambient temperature using an unfiltered Pen-Ray lamp. Oxides of nitrogen and water were formed, although most of the starting material was recovered unchanged.

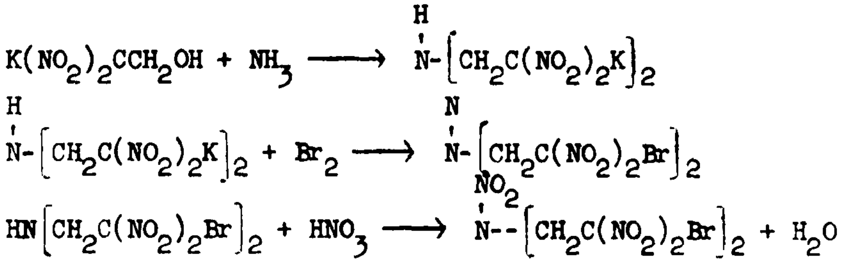
The reaction of sodium phenoxide with tetrafluorohydrazine in methanol was also studied briefly. A dark-green solid that contained only a trace of nitrogen was isolated.

F. DERIVATIVES OF 2,2-DINITRO-2-FLUOROETHANOL* (O.S. Schaeffler)

2,2-Dinitro-2-fluoroethanol, which can be synthesized readily by the aqueous fluorination of alkali salts of dinitroethanol,** is a convenient starting material for the synthesis of new high-energy monomers and plasticizers. Thus, bis-2,2-dinitro-2-fluoroethyl formal is being examined as a polyurethane plasticizer on other programs. The reaction of 2,2-dinitro-2-fluoroethanol with vinyl acetate was carried out to prepare bis(2,2-dinitro-2-fluoroethyl) acetal, another potential plasticizer. Methylene chloride was used as the solvent, and sulfuric acid and mercuric oxide were used as the catalysts. The product was a liquid, b.p. 118.5 to 119°C/0.5 mm Hg.

The first monomer based on this energetic alcohol, 2,2-dinitro-2-fluoroethyl acrylate, has been prepared both by the reaction of 2,2-dinitro-2-fluoroethanol and acrylyl chloride and by the esterification of 2,2-dinitro-2-fluoroethanol and acrylic acid in polyphosphoric acid.

bis(2-Fluoro-2,2-dinitroethyl)nitramine has been synthesized by the following reaction sequence:



$$K(NO_2)_2CCH_2OH + NH_3 \longrightarrow \overset{H}{N}\text{-}\left[CH_2C(NO_2)_2K\right]_2$$

$$\overset{H}{N}\text{-}\left[CH_2C(NO_2)_2K\right]_2 + Br_2 \longrightarrow \overset{N}{N}\text{-}\left[CH_2C(NO_2)_2Br\right]_2$$

$$HN\left[CH_2C(NO_2)_2Br\right]_2 + HNO_3 \longrightarrow \overset{NO_2}{N}\text{--}\left[CH_2C(NO_2)_2Br\right]_2 + H_2O$$

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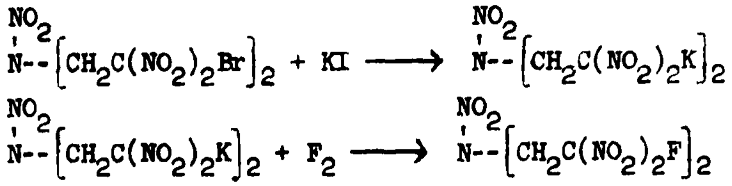
* Aerojet-General Reports No. 0235-01-9, 13 January 1961; No. 0235-01-10, 14 April 1961 (Confidential).

** Aerojet-General Report No. 0235-01-6, 18 April 1960, p. 3 (Confidential).



$$\overset{NO_2}{\overset{|}{N}}\text{--}\left[CH_2C(NO_2)_2Br\right]_2 + KI \longrightarrow \overset{NO_2}{\overset{|}{N}}\text{--}\left[CH_2C(NO_2)_2K\right]_2$$

$$\overset{NO_2}{\overset{|}{N}}\text{--}\left[CH_2C(NO_2)_2K\right]_2 + F_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}\text{--}\left[CH_2C(NO_2)_2F\right]_2$$

The dipotassium salt of bis(2,2-dinitroethyl)nitramine was prepared by the method of Klager,* which consists of the Mannich reaction of potassium dinitroethanol with ammonia, followed by bromination, nitration, and debromination. The product of the reaction was suspended in water and fluorinated at 18 to 20°C to give bis(2-fluoro-2,2-dinitroethyl)nitramine. This material was a white solid, which melted at 84 to 85°C after a recrystallization from methylene chloride.

G. HYDRAZINE SALTS OF NITRAMINES (K. Baum)

1. Discussion

Hydrazine perchlorate and hydrazine nitroformate are currently receiving considerable attention as solid oxidizers for high-specific-impulse composite propellants. The former salt, however, has rather poor impact stability, while the latter has poor thermal stability. Another class of salts which has been overlooked for this purpose makes use of the acidic hydrogens of primary nitramines. This area was investigated briefly in the hope of overcoming these drawbacks.

The hydrazine salt of _n_-butylnitramine was used as a model compound. Equivalent amounts of hydrazine and _n_-butylnitramine were mixed in methanol and the solution was stripped. The product, mp 75-78°C, had an impact stability equivalent to RDX, and differential thermal analysis (DTA) showed an exotherm at 180°C.

When this reaction was extended to methylenedinitramine, the dihydrazine salt was formed. The impact stability of this salt was 55 cm/2 kg (vs 30 to 35 cm for RDX), and the DTA showed an endotherm at 130°C and no

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*K. Klager, J. Org. Chem., 23, 1519 (1958).

exotherm. The compound underwent an apparent crystalline phase change at 110°C, and melted and sublimed at 147°C. The crystal density was 1.69 g/cc.

2. Experimental

a. Hydrazine Salt of n-Butylnitramine

A solution of 0.02 mole of hydrazine in 30 ml of methanol was added to a solution of 2.36 g (0.02 mole) of n-butylnitramine in 30 ml of methanol. The resulting homogeneous solution was evaporated to dryness using an aspirator to give a white solid which was dried under vacuum. The product, mp 75 to 78°C, had an impact stability of 35 cm/2 kg. The DTA showed an exotherm at 180°C.

b. Dihydrazine Salt of Methylenedinitramine

A solution of 0.150 mole of hydrazine in 25 ml of methanol was added, in drops, to 10.2 g (0.075 mole) of methylenedinitramine in 75 ml of methanol. A slightly yellow precipitate separated, and was filtered, washed with cold methanol, and dried under vacuum. The product consisted of 12.8 g (86% yield) mp 146°C (with sublimation), phase change at 110°C; density 1.69 g/ml; impact stability 55 cm/2 kg; DTA gave an endotherm at 130°C.

An analytical sample was prepared by dissolving a sample of the salt in water and slowly precipitating it by the addition of methanol.

Anal. calc'd for $CH_{12}N_8O_4$: C, 6.00; H, 6.00; N, 56.00
Found: C, 5.60; H, 6.85; N, 56.80.

III. SUMMARY AND CONCLUSIONS

A. REACTIONS OF DIFLUORAMINE

1. gem-Difluoramines may be prepared by the reaction of HNF_2 and sulfuric acid with a variety of ketones, aldehydes, and acetylenes.

2. Most simple ketones (acetone, cyclopentanone, and 3-pentanone) react readily to give good yields of the products, but structural features pose some limitations (acetophenone and camphor).

3. The reactions of diketones are complex. 1,4-Cyclohexanedione behaves normally but open-chain 1,4-diketones (acetonylacetone) result in cyclization. 1,2- and 1,3-diketones also behave abnormally.

4. A single halogen α- to the ketone function (chloroacetone) does not interfere with the reaction. An α-hydroxyl group (acetol) enters into the reaction. A lactone is formed from a γ-keto acid (levulinic acid).

5. Polynitro ketones (3-[trinitromethyl]cyclohexanone, 5,5,5-trinitro-2-pentanone, and 5,5-dinitro-2-hexanone) do not react, but reaction does occur with certain β-nitro ketones (5-nitro-2-hexanone is normal, 5-methyl-5-nitro-2-hexanone is abnormal).

6. Acid-catalyzed Michael additions occur with acrylic acid (to give β-difluoramino propionic acid) and methyl vinyl ketone (to give 1,3,3-tris[difluoramino]butane).

7. The products obtained from aldehydes depend markedly on the strength of the sulfuric acid used. <u>gem</u>-Difluoramines are obtained with fuming sulfuric acid, but α,α'-bis(difluoramino)ethers are often encountered with concentrated sulfuric acid. bis(Difluoramino)methane and 1,1-bis(difluoramino)propane have been prepared from formaldehyde and propionaldehyde, respectively.

8. Acetylenes which react to give <u>gem</u>-difluoramines include propargyl chloride (to give 1-Chloro-2,2-bis[difluoramino]propane), 1-hexyne (to give 2,2-bis[difluoramino]hexane), and 3-hexyne (to give 3,3-bis[difluoramino]hexane).

B. AQUEOUS FLUORINATION

1. Alkylureas are selectively fluorinated at N-H bonds in aqueous solution. Two products are often formed: N-alkyl-N',N'-difluoroureas and alkyl difluoramines by the fluorinative cleavage of the N-alkylamino-carbonyl linkage. N,N'-Dialkylureas give predominately, the alkyl difluoramines.

2. Arylureas are cleaved at the aryl-nitrogen bond to give difluorourea, and a complex mixture of materials.

3. Fluorination of N-substituted acetamides and formamides is not as selective as the ureas. N-Methyl amides undergo only N-H fluorination but higher alkyl groups are attacked at C-H linkages also.

4. N,N-Difluorourea is formed during the fluorination of cyanamide and guanidine sulfate.

C. PREPARATION AND REACTIONS OF N-FLUOROCARBAMATES

1. Fluorination of alkyl carbamates in aqueous solution leads to a mixture of alkyl N-fluorocarbamates and HNF_2. Evidence indicates that the source of HNF_2 is the alkyl N,N-difluorocarbamates, which are hydrolytically unstable.

2. The alkyl N-fluorocarbamates react with alkalis at 0 to 10°C to form solutions of the salts from which the starting materials can be recovered upon acidification. Solutions of the salts are not stable at 20 to 25°C. Among the decomposition products is sodium fluoride.

3. The salts of alkyl N-fluorocarbamates undergo alkylation ($\{CH_3\}_2SO_4$), carbethoxylation ($ClCO_2C_2H_5$), and halogenation (Cl_2, Br_2) at the nitrogen atom.

4. Reaction of $ClNFCO_2C_2H_5$ with sodium hypochlorite is a simple method for the preparation of Cl_2NF. However, it has not been possible to isolate Br_2NF from the reaction of ethyl N-fluorocarbamate and sodium hypobromite, or BrClNF from the reaction of ethyl N-bromo-N-fluorocarbamate with sodium hypochlorite.

5. Although earlier work demonstrated that N-fluoro-N-nitro compositions can be formed by fluorination of the salts of primary nitramines, this former class of compounds is not formed by the nitration of alkyl N-fluorocarbamates by ethyl nitrate and acid.

6. Displacement of fluorine from nitrogen is noted in the reaction of diethylamine with ethyl N-fluorocarbamate to yield N-carbethoxy-N',N'-diethyl hydrazine.

7. Unidentified materials were obtained from the reaction of PCl_5 with ethyl N-fluorocarbamate.

8. Attempts to use N-fluorocarbamates as fluorinating agents have not been successful.

9. Attempts to prepare dialkyl N,N'-difluorohydrazodicarboxylate from the salt of ethyl N-fluorocarbamate and ethyl N-bromo-N-fluorocarbamate gave, instead, diethyl N-fluoriminodicarboxylate. The same product was obtained in the attempted preparation of diethyl perfluorotriazenedicarboxylate from Cl_2NF and two moles of the salt of ethyl N-fluorocarbamate.

D. REACTION OF DICHLOROFLUORAMINE WITH N_2F_4

A reaction occurs between Cl_2NF and N_2F_4 at 0°C. A product is formed which decomposes upon standing for several hours at room temperature. It has not been possible to establish whether or not this material is the desired F_2NNFCl.

E. REACTION OF TETRAFLUOROHYDRAZINE WITH ANIONS

1. Reaction of sodium 2-propanenitronate and N_2F_4 in the presence of sodium nitrite gave 2,2-dinitropropane.

2. An uncharacterized solid, containing only a trace of nitrogen, is formed in the reaction of N_2F_4 with sodium phenoxide.

F. DERIVATIVES OF 2,2-DINITRO-2-FLUOROETHANOL

1. bis(2,2-Dinitro-2-fluoroethyl)acetal and 2,2-dinitro-2-fluoroethyl acrylate have been prepared by the reactions of fluorodinitroethanol with vinyl acetate and acrylyl chloride, respectively.

2. The potential plasticizer, bis-(2-fluoro-2,2-dinitroethyl)-nitramine, has been prepared.

G. HYDRAZINE SALTS OF NITRAMINES

Two hydrazine salts of nitramines were prepared. The salt of n-butyl-nitramine served as a model for the preparation of the dihydrazine salt of methylene-dinitramine. The latter compound appeared attractive as a solid oxidizer for composite propellants.

IV. RECOMMENDATIONS FOR FUTURE WORK

A. REACTIONS OF DIFLUORAMINE

1. The scope of the reaction of HNF_2-sulfuric acid with ketones, aldehydes, and acetylenes should be investigated further. The influence of various substituents and structural features upon the reaction should be studied to ascertain the mechanistic implications.

2. The chemistry of gem-difluoramines should be studied to ascertain the chemical behavior of the compounds. Elucidation of this behavior will enable subsequent transformations to be carried on so that new, useful materials can be prepared.

3. Solvents other than concentrated and fuming sulfuric acids are desirable. Therefore, efforts should be devoted to a study of various solvent systems.

B. AQUEOUS FLUORINATIONS

1. The effects of various substituents and structural features upon the course of aqueous fluorination should be examined further. This study should greatly extend the scope of the reaction and enable its extensive use in the preparation of NF compositions.

2. The novel fluorinative degradation noted with substituted ureas and carbamates should be extended to determine applicability for the preparation of compounds with high NF_2 content.

3. The chemistry of the partially fluorinated compounds obtained by the aqueous fluorination technique, such as ethyl N-fluorocarbamate, requires more thorough study. Information obtained to date suggests that this study may lead to new or attractive alternate routes to NF compounds.

C. PREPARATION OF CHLOROTRIFLUOROHYDRAZINE

Additional effort should be devoted to the reaction of tetrafluorohydrazine and dichlorofluoramine to establish conclusively whether or not chlorotrifluorohydrazine is a product. If chlorotrifluorohydrazine is present, the physical properties of the material should be thoroughly characterized and its chemistry investigated.

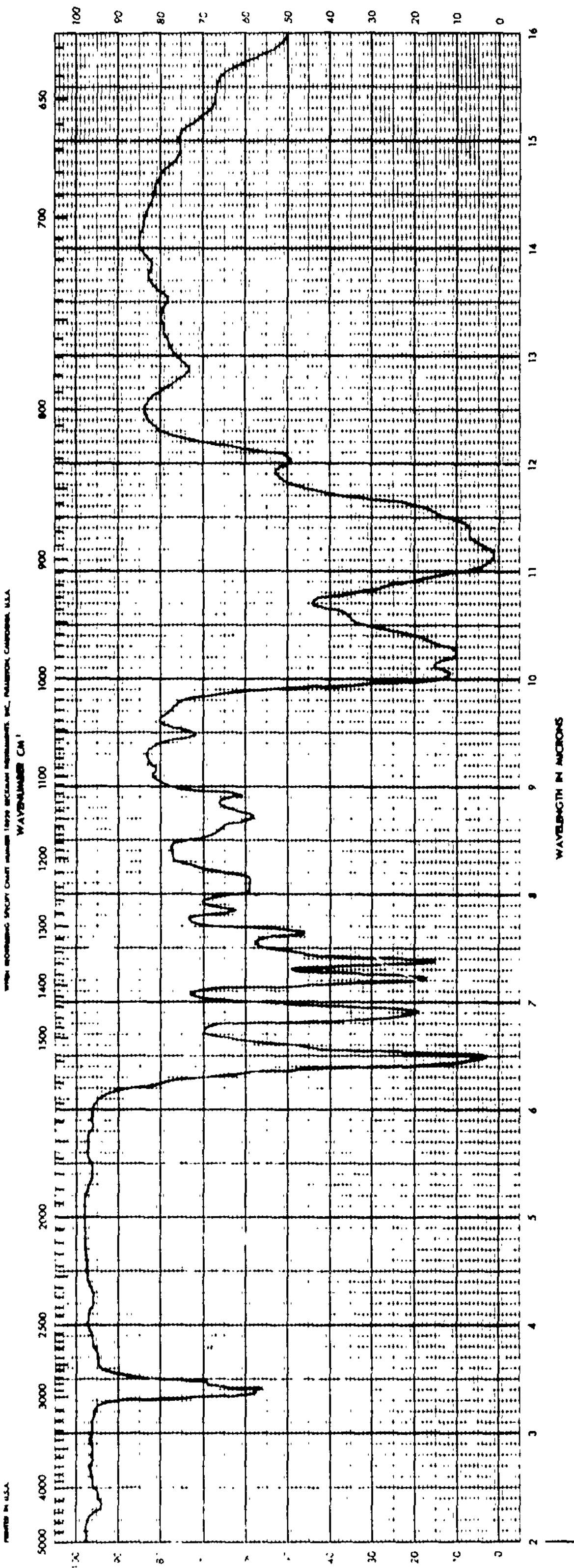


Figure 1

)-Nitro-2,2-bis(Difluoramino)hexane

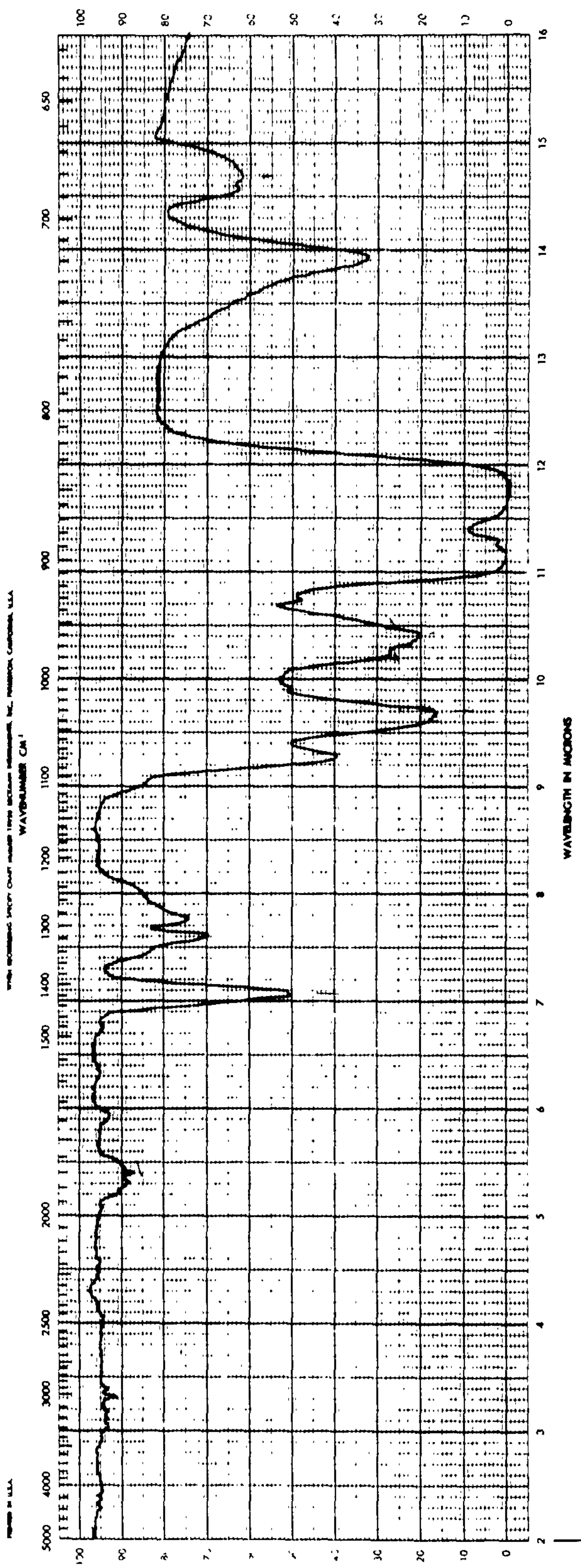
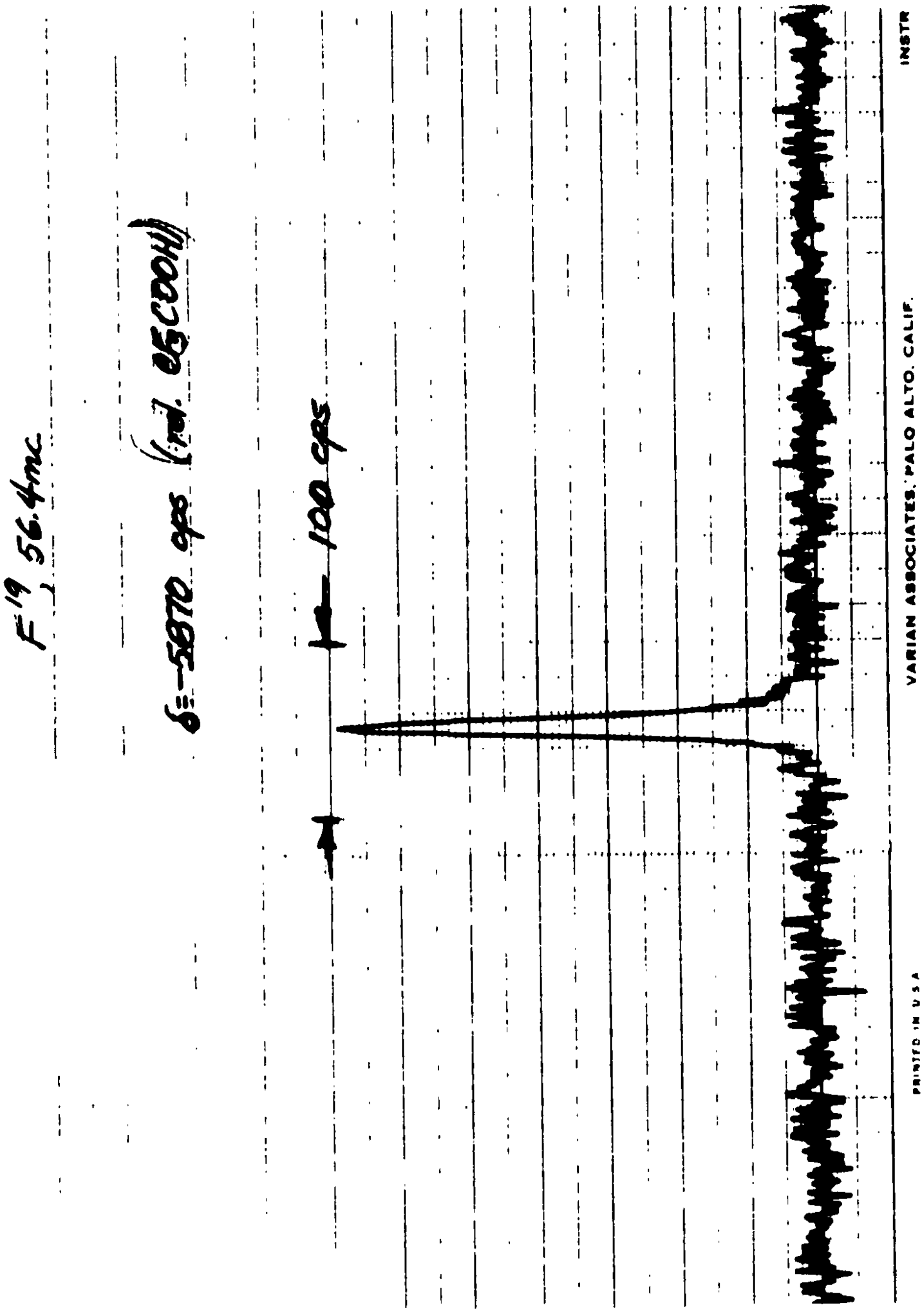


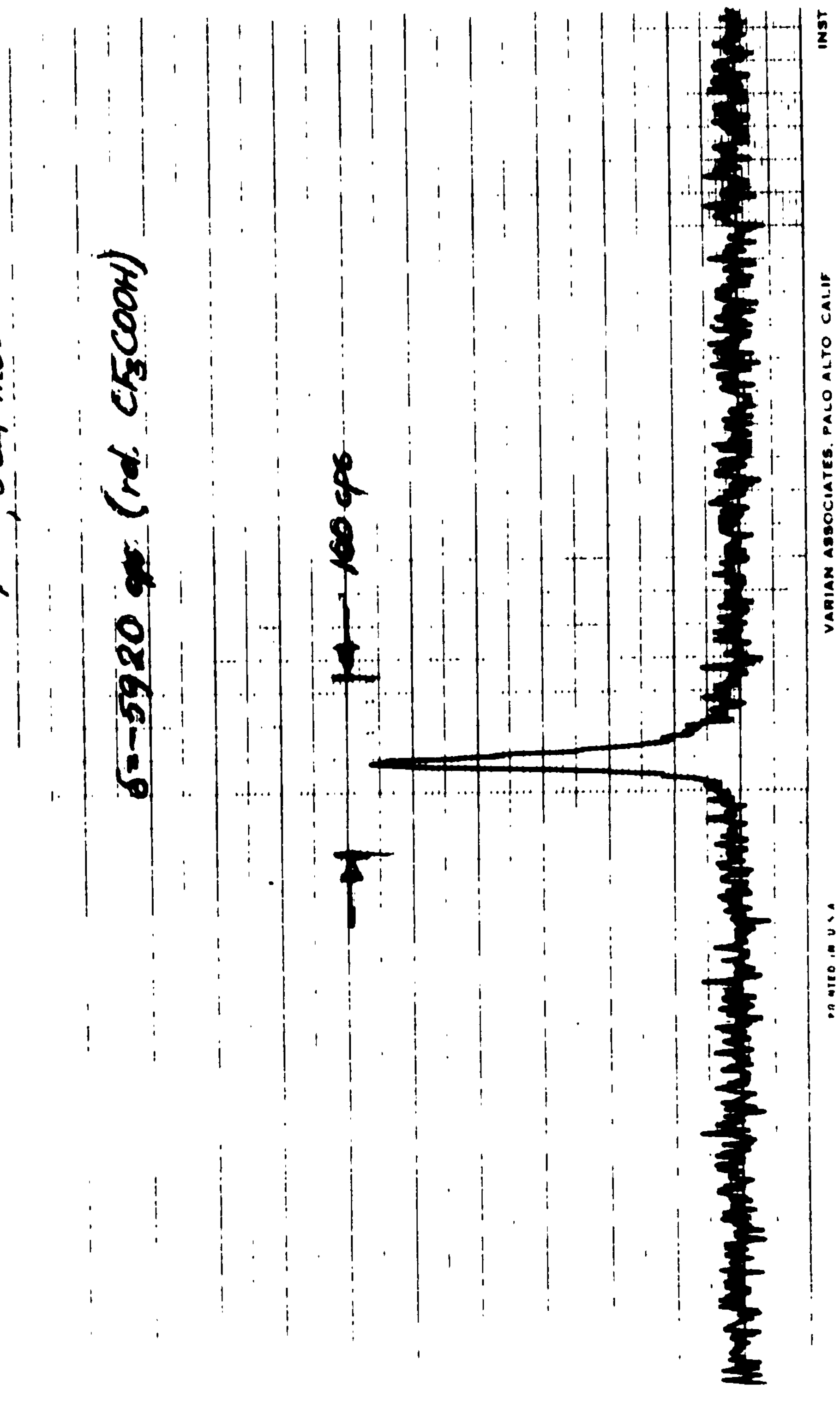
Figure 2

bis(Difluoramino)methane



F^{19} NMR Spectrum of 2,2-bis(Difluoramino)hexane

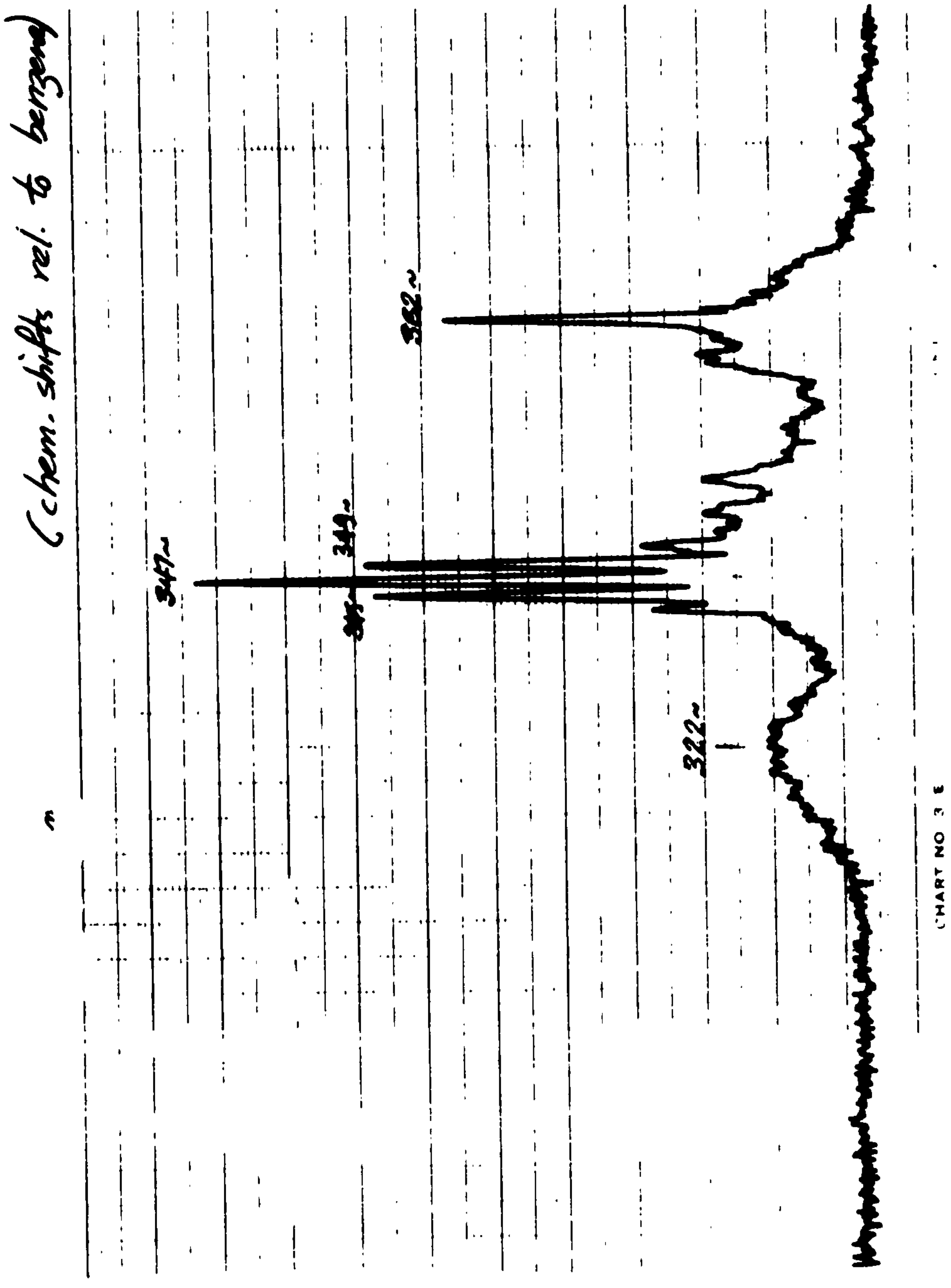
Figure 3



F^{19}, 564 mc.

$\delta = -5920$ cps (rel. CF_3COOH)

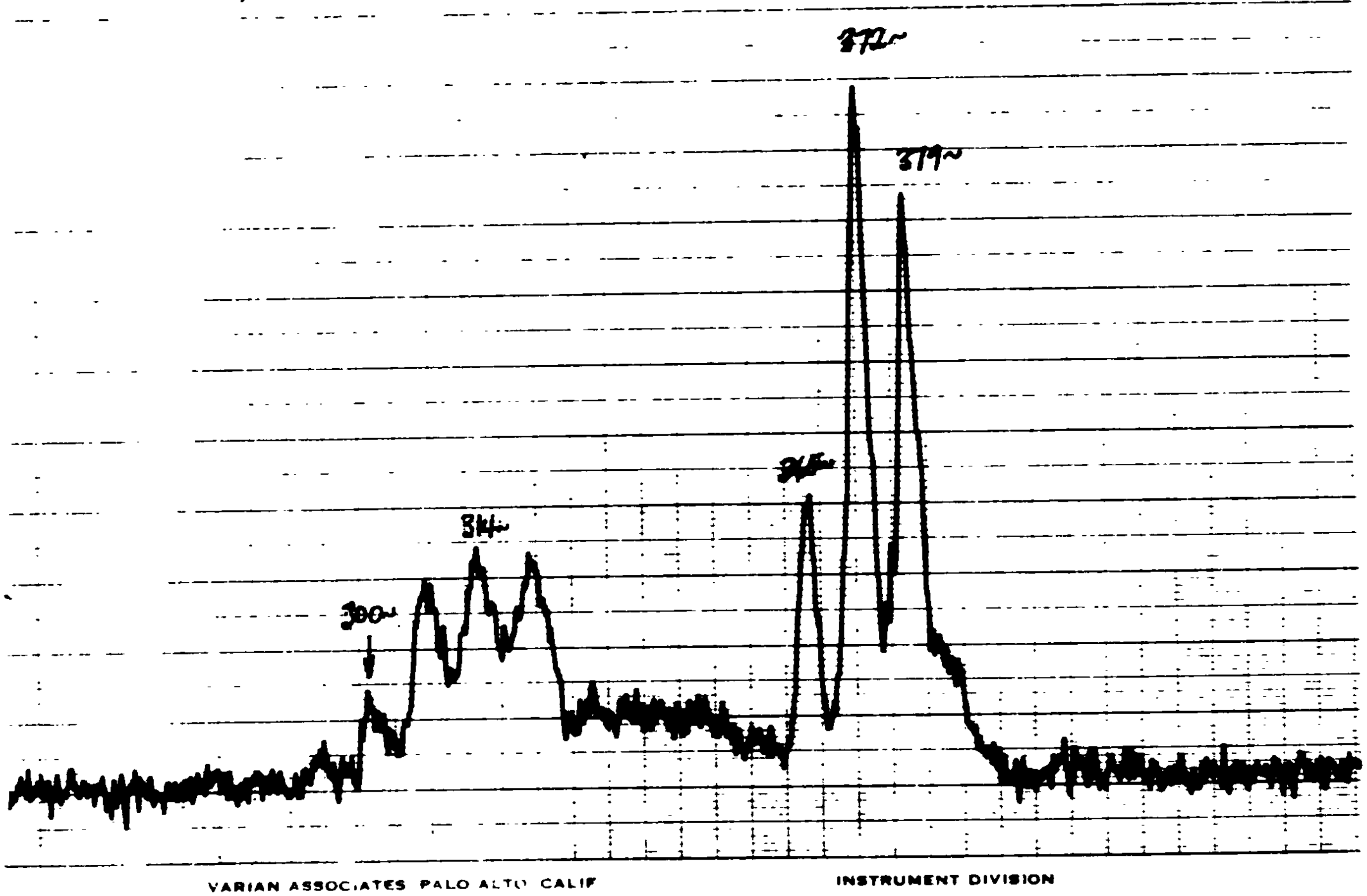
F^{19} NMR Spectrum of 3,3-bis(Difluoramino)hexane



H' NMR Spectrum of 2,2-bis(Difluoroamino)hexane

Figure 5

H^1 @ 56.4 mc. (chem. shifts rel. to benzene)



H' NMR Spectrum of 3,3-bis(Difluoroamino)hexane

Figure 6

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