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REPORT NO. 2945 (SUMMARY)
PERIOD COVERED: 1 OCTOBER 1963-30 SEPTEMBER 1964

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RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT TO

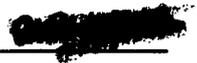
OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

CONTRACT Nonr 2855(00)
ARPA ORDER NO. 170, AMENDMENT NO. 6
PROJECT CODE 4610

OCTOBER 1964

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AEROJET-GENERAL CORPORATION
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October 1964

Report No. 2945

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

By:

K. Baum
J. M. Cavallo
F. J. Gerhart

V. Grakauskas
A. H. Remanick
O. S. Schaeffler

Analytical Support:

C. L. Deuel
K. Inouye

H. Nelson

A Report To

**OFFICE OF NAVAL RESEARCH
and
ADVANCED RESEARCH PROJECTS AGENCY**

Contract Nonr 2655(00)
ARPA Order No. 170, Amendment No. 6
Project Code 4910

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Report No. 2945

This report summarizes the research carried out under Contract Nonr 2655(00), ARPA Order No. 170, Amendment No. 6, Project Code 4910, during the period 1 October 1963 through 30 September 1964.

AEROJET-GENERAL CORPORATION

L. R. Rapp / M. Zinchen

L. R. Rapp, Manager
Chemical Products Division

Page 11

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Report No. 2945

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.

Page 111

CONFIDENTIAL

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Report No. 2945

CONTENTS

	<u>Page</u>
I. INTRODUCTION _____	1
II. TECHNICAL DISCUSSION _____	1
A. Reactions of Difluoramine _____	1
B. Direct Fluorination _____	13
C. Fluoroammonium Salts _____	34
III. SUMMARY _____	38
A. Reactions of Difluoramine _____	38
B. Direct Fluorination _____	39
C. Fluoroammonium Salts _____	39
IV. CONCLUSIONS AND RECOMMENDATIONS _____	40
V. PERSONNEL _____	41
	<u>Figure</u>
Infrared Spectrum of α -Bromo- α,α -bis(difluoramino)toluene _____	1
Proton NMR Spectrum of α -Bromo- α,α -bis(difluoramino)toluene _____	2
Fluorine Spectrum of α -Bromo- α,α -bis(difluoramino)toluene _____	3
Infrared Spectrum of 1-Chloro-1,1-bis(difluoramino)propane _____	4
Proton NMR Spectrum of 1-Chloro-1,1-bis(difluoramino)propane _____	5
Fluorine NMR Spectrum of 1-Chloro-1,1-bis(difluoramino)propane _____	6
Proton NMR Spectrum of 1-(N-fluoro-N-formylamino)-3-difluoraminopropane _____	7
Proton NMR Spectrum of <u>n</u> -Difluoraminobutane _____	8
Fluorine Spectrum of <u>n</u> -Difluoraminobutane _____	9

CONFIDENTIAL

Report No. 2945

CONTENTS (cont.)

APPENDIX - DIRECT FLUORINATION OF ALKYL CARBAMATES IN SOLUTION

	<u>Table</u>
Alkyl N-Fluorocarbamates, NHFCO_2R _____	A-1
Fluorine and Proton NMR Spectra of Alkyl N-Fluorocarbamates, NHFCO_2R _____	A-2
Alkyl N,N-Difluorocarbamates, $\text{NF}_2\text{CO}_2\text{R}$ _____	A-3
Fluorine and Proton NMR Spectra of Alkyl N,N-Difluorocarbamates, $\text{NF}_2\text{CO}_2\text{R}$ _____	A-4
	<u>Figure</u>
Direct Fluorination Apparatus _____	A-1

Distribution List

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Report No. 2945

I. INTRODUCTION

This report summarizes the research carried out under Contract NOnr 2655(00), ARPA Order No. 170, Project Code 4910, during the period 1 October 1963 through 30 September 1964. The work performed from 1 October 1963 to 3 June 1964 has been reported in Aerojet-General Quarterly Reports, 0235-01-18, -19, -20, and will be summarized here and referenced. Experimental details will be included only for the period 1 July 1964 to 30 September 1964. 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 1162, 1318, 1509, 1685, 1877, 2099, 2381, and 2730.

During the past year, research has continued on the reactions of difluoramine and on direct fluorination of nitrogenous compounds in solution, with the following main objectives: (1) to synthesize new types of high-energy NF compounds; (2) to improve synthetic techniques for the preparation of known NF compounds; and (3) to obtain a greater practical and theoretical understanding of NF chemistry.

The study on fluoroammonium salts has been also continued aiming specifically to the establishment of preparative techniques for the synthesis of fluoroammonium perchlorate, a model compound representing a novel class of inorganic NF oxidizers.

II. TECHNICAL DISCUSSION

A. REACTIONS OF DIFLUORAMINE (K. Baum)

1. Introduction

Difluoramine has proven to be a versatile reagent for the synthesis of a variety of NF compounds, the most useful of which have been the

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II Technical Discussion, A (cont.)

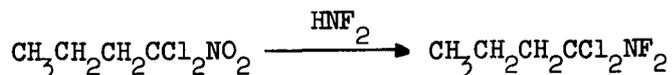
Report No. 2945

gem-difluoramines. During the past year, the major effort on this program has been devoted to the investigation of new leaving groups for difluoramine reactions. These reactions could yield new types of NF compounds, potentially useful in propellants, such as 1,1,1-tris(difluoramino)alkanes.

2. Discussion

a. Halonitro Compounds

It was found previously that the reaction of vinylidene chloride with difluoramine in fuming sulfuric acid gave 1,1-dichloro-1-difluoraminoethane, 1-chloro-1,1-bis(difluoramino)ethane, and a small amount of another material, the proton NMR spectrum of which was consistent with the 1,1,1-tris(difluoramino)ethane structure.* However, attempts to reproduce this experiment were unsuccessful. Because of experimental difficulties resulting from the high volatility of these products, the reaction was applied to higher homologues. Since it had previously been shown that nitro groups can be removed in the presence of difluoramine and sulfuric acid,** the reaction of 1,1-dichloro-1-nitrobutane with difluoramine was attempted with the objective of preparing 1,1-dichloro-1-(difluoramino)butane.*** This compound was synthesized in 61% yield after 2 hours when the reaction was conducted at ambient temperature using fuming sulfuric acid.



An unsuccessful attempt was made to replace the chlorine atoms by extending the reaction time to 24 hours; only 1,1-dichloro-1-(difluoramino)butane was isolated.

1,1-Dibromo-1-nitrobutane, on the other hand, underwent the replacement of the nitro group and one bromine with relative ease.**** The reaction of this compound with refluxing difluoramine in fuming sulfuric acid for 4 hours gave a mixture of 1,1-dibromo-1-difluoraminobutane and 1-bromo-1,1-bis(difluoramino)butane. 1-Bromo-1,1-bis(difluoramino)butane was isolated, however,

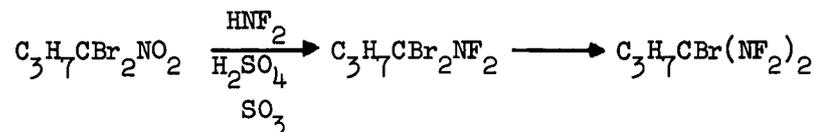
* Aerojet-General Report 2730, October 1963, p. 4 (Confidential).
** Aerojet-General Report 0235-01-11, 14 July 1961, p. 3 (Confidential).
*** Aerojet-General Report 0235-01-18, January 1964, p. 1 (Confidential).
**** Aerojet-General Report 0235-01-19, April 1964, p. 1 (Confidential).

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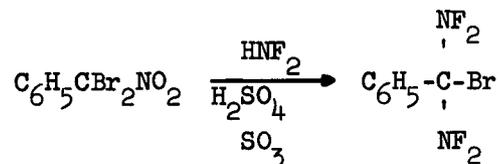
II Technical Discussion, A (cont.)

Report No. 2945

when this reaction was carried out for 2 hours at the reflux temperature of difluoramine, followed by 2 hours at ambient temperature under autogenous pressure. An unsuccessful attempt was made to replace the remaining bromine, and the same product was obtained when the reaction time was extended to 24 hours at ambient temperature. However, no extensive investigation was made of the effect of reaction conditions.

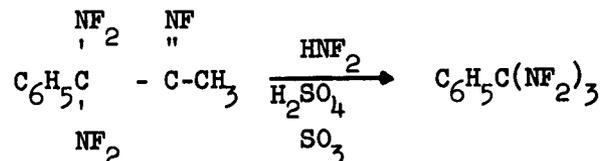


This reaction was attempted using α, α -dibromo- α -nitro-toluene* as the starting material. In this case, the bromines of the intermediate α -bromodifluoramines should be more labile because of activation by the phenyl group. The reaction was initially carried out using refluxing difluoramine and fuming sulfuric acid, with a reaction period of 4 hours. The product, obtained in 72% yield, was α -bromo- α, α -bis(difluoramino)toluene, identified by elemental analysis, infrared (Figure 1), proton (Figure 2), and fluorine (Figure 3) NMR spectra.



This reaction is being repeated under more forcing conditions.

The expected product, α, α, α -tris(difluoramino)toluene has recently been synthesized by the cleavage of a fluorimino group in the presence of difluoramine and fuming sulfuric acid**:



* G. Ponzio, Gazz. chim. ital., 38 II, 418 (1908).

** Quarterly Progress Report on ARPA Products, Rohm & Haas Co., Report No. P-64-12, July 21, 1964, p. 2 (Confidential).

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II Technical Discussion, A (cont.)

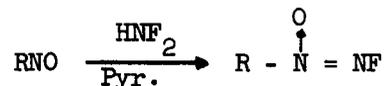
Report No. 2945

The present approach has the advantage of using readily available starting materials.

1-Bromo-1,1-dinitrobutane was synthesized in order to assess the reactivity of this general class of compounds. However, when this compound was treated with difluoramine in fuming sulfuric acid for 20 hours at ambient temperature, only unreacted starting material was recovered.*

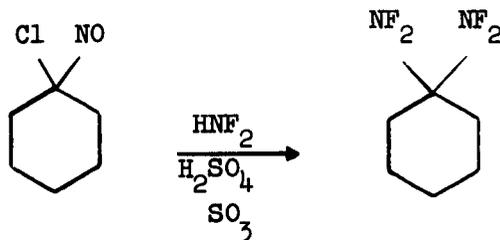
b. Nitroso Compounds

Nitroso compounds have been reported to react with difluoramine and pyridine to form N-fluoroazoxy compounds:**



No work has been reported on the use of nitroso groups as leaving groups for acid-catalyzed difluoramine reactions.

When 1-chloro-1-nitrosocyclohexane*** was added to refluxing difluoramine in fuming sulfuric acid, the blue color of the starting material disappeared instantaneously, and a gas was evolved. Workup after 2 hours yielded only 1,1-bis(difluoramino)cyclohexane****



The nitroso group may be removed by direct protonation, followed by loss of HNO, or possibly through the formation of a fluoroazoxy intermediate that undergoes protonation and cleavage.

* Aerojet-General Report No. O235-01-19, April 1964, p. 2 (Confidential).

** Quarterly Progress Report on ARPA Projects, Rohm & Haas Co., No. P-61-21, 25 October 1964, p. 1 (Confidential).

*** E. Müller, H. Metzger, and D. Fries, Ber., 87, 1454 (1954).

**** Aerojet-General Report O235-01-19, April 1964, p. 2 (Confidential).

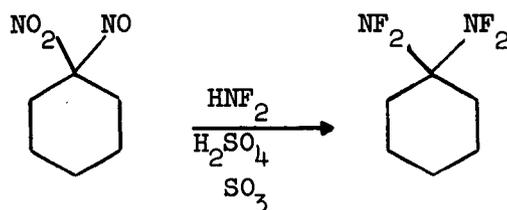
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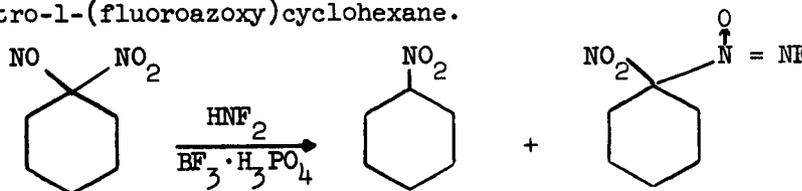
II Technical Discussion, A (cont.)

Report No. 2945

Under the same experimental conditions, 1-nitro-1-nitrosocyclohexane* was treated with difluoramine. The only product that was isolated after a 2-hour reaction period was 1,1-bis(difluoramino)cyclohexane. A possible intermediate in this reaction is the α -nitrodifluoramine. In the hope of isolating an intermediate, the reaction was repeated but was quenched with ice 5 min after addition of the starting material was completed. Again, the only product isolated was 1,1-bis(difluoramino)cyclohexane:



This reaction was repeated using a milder catalyst, the boron trifluoride complex of phosphoric acid, instead of sulfuric acid. When a mixture of 1-nitro-1-nitrosocyclohexane, difluoramine, and the boron trifluoride complex of phosphoric acid was allowed to reflux for 45 min, two products were isolated; nitrocyclohexane and 1-nitro-1-(fluoroazoxy)cyclohexane.**



These products might be formed from a common intermediate, the nitroso difluoramine adduct. The loss of HF would give the fluoroazoxy compound, whereas elimination of NONF₂ would give nitrocyclohexane. The latter reaction is essentially the nitrosation of difluoramine by 1-nitro-1-nitrosocyclohexane.

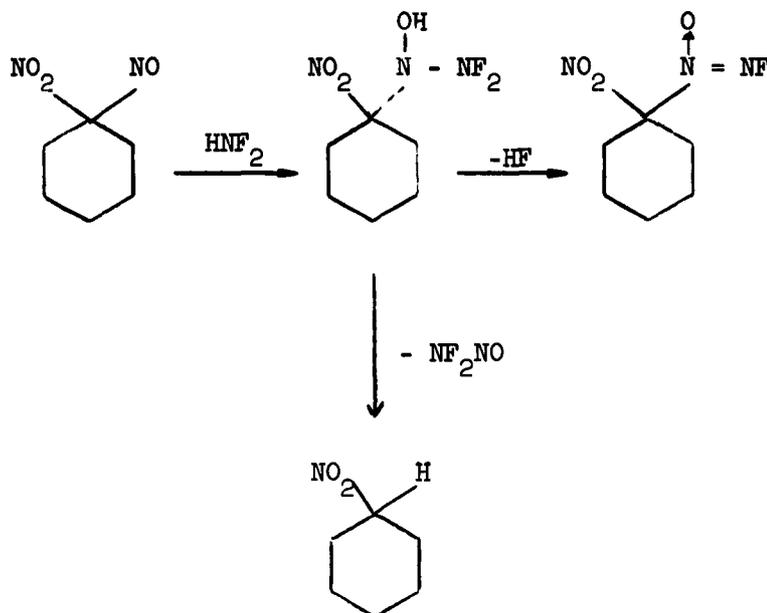
* Aerojet-General Report 0235-01-19, April 1964, p. 3 (Confidential).

** Aerojet-General Report 0235-01-20, July 1964, p. 2 (confidential).

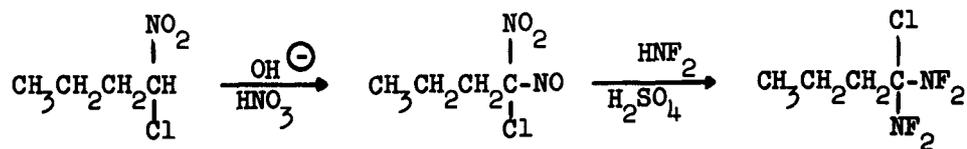
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II Technical Discussion, A (cont.)

Report No. 2945



The reactions of 1-halo-1-nitro-1-nitrosoalkanes with difluoramine were also studied.* To prepare 1-chloro-1-nitro-nitrosobutane, 1-chloro-1-nitrobutane was dissolved in aqueous alkali at 0 to 5°C and sodium nitrite and sulfuric acid were added. A dark-blue oil separated, which, however, was too unstable for vacuum distillation. In one case the material fumed off after standing for several minutes at room temperature. Subsequently the nitrosation product was dissolved in pentane as soon as it was formed, and was stored at -80°C until it was reacted with difluoramine. When this blue oil was reacted with refluxing difluoramine in fuming sulfuric acid, 1-chloro-1,1-bis(difluoroamino)butane was formed.



*Aerojet-General Report 0235-01-20, July 1964, p. 1 (Confidential).

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II Technical Discussion, A (cont.)

Report No. 2945

This reaction sequence was recently used to prepare 1-chloro-1,1-bis(difluoramino)propane from 1-chloro-1-nitropropane. The infrared, and proton and fluorine NMR spectra of 1-chloro-1,1-bis(difluoramino)propane are shown in Figures 4, 5, and 6, respectively.

The nitrosation of 1-bromo-1-nitropropane, followed by the reaction of the product with difluoramine in fuming sulfuric acid gave a complex mixture of products. The only one of these compounds that has yet been identified is propionitrile.

Alkyl nitrites might be expected to react with difluoramine either as alkylating agents, giving alkyl difluoramines, or as nitrosating agents, giving alcohols and NF_2NO . The former course would be useful in the preparation of propellant ingredients. When n-octyl nitrite was added to refluxing difluoramine,* with no catalyst, a transient purple color formed, indicative of NF_2NO . When the difluoramine was removed, n-octanol remained. Similarly, t-butyl nitrite gave t-butanol.



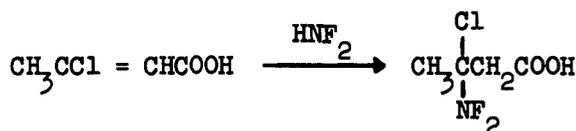
c. Miscellaneous Difluoramine Reactions

The reaction of cis-3-chlorocrotonic acid with difluoramine was studied with the objective of synthesizing 3,3-bis(difluoramino)butyric acid. This model reaction would give a route to a new, potentially useful class of compounds; acetoacetic esters did not undergo the expected difluoramine reaction. When cis-3-chlorocrotonic acid was treated with refluxing difluoramine in fuming sulfuric acid, 3-chloro-3-(difluoramino)butyric acid was isolated.** When this reaction was repeated at ambient temperature in a closed reactor, the same product was formed. The inductive effect of the carboxyl, possibly protonated, could be responsible for inhibiting displacement of the chlorine.

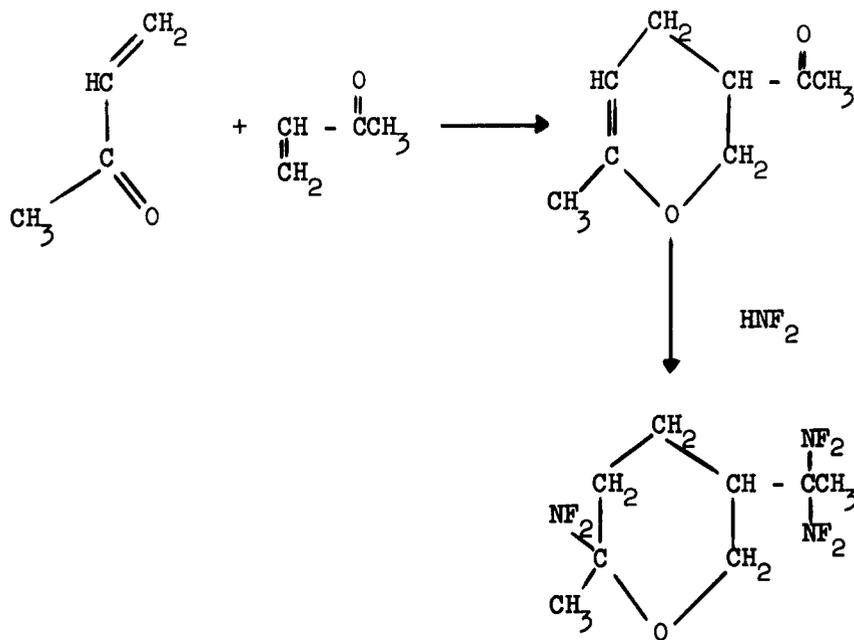
* Aerojet-General Report 0235-01-20, July 1964, p. 3 (Confidential).

** Aerojet-General Report 0235-01-18, January 1964, p. 2 (Confidential).

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Although the reaction of methyl vinyl ketone with difluoramine in concentrated sulfuric acid is known to give 1,3,3-tris(difluoramino)-butane,* this reaction was re-examined using fuming sulfuric acid as the solvent because of the unexpected results that were obtained with the chlorinated analog under these conditions.** The product was found to contain, in addition to 1,3,3-tris(difluoramino)-butane, 2-methyl-2-difluoramino-5-[1,1-bis(difluoramino)-ethyl]-tetrahydropyran.*** This material might be formed either by the reaction of the intermediate, 3,3-bis(difluoramino)1-butene, with methyl vinyl ketone or by the acid-catalyzed self-condensation of the latter, followed by reaction with difluoramine.



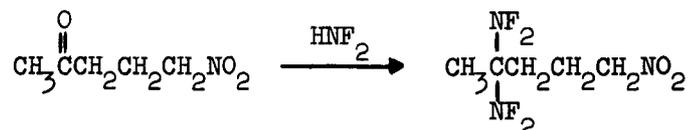
* Aerojet-General Report 0235-01-11, July 1961, p. 2 (Confidential).
 ** Aerojet-General Report 2730, October 1963, p. 5 (Confidential).
 *** Aerojet-General Report 0235-01-18, January 1964, p. 3 (Confidential).

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II Technical Discussion, A (cont.)

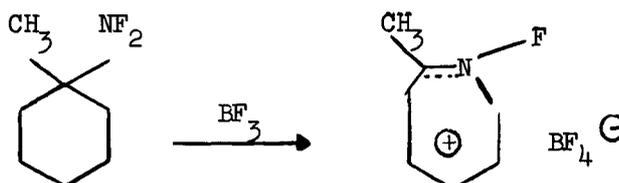
Report No. 2945

5-Nitro-2-pentanone was also treated with difluoramine in fuming sulfuric acid to give 5-nitro-2,2-bis(difluoramino)pentane.* The halogenation of this compound and subsequent difluoramine reactions will be studied if the above model reactions are successful.



d. Reactions of Difluoramino Compounds

The reaction of 1-methyl-1-difluoraminocyclohexane with boron trifluoride has been shown to yield an immonium fluoborate as follows:**



The analogous salt derived from t-butyldifluoramine was also prepared and identified by elemental analysis. The reaction was conducted by bubbling boron trifluoride through a pentane solution of t-butyldifluoramine at -80°C , and resulted in a 59.5% yield of N-methyl-N-isopropylidene-N-fluoroammonium fluoborate. The starting material, t-butyldifluoramine, was prepared in 63% yield from isobutylene and difluoramine in the presence of the boron trifluoride complex of phosphoric acid.

The rearrangement of secondary and tertiary alkyl difluoramines to immonium ions in concentrated sulfuric acid has been reported.*** This study has been extended to a primary derivative, ethyl difluoramine. The reaction of ethyl difluoramine with sulfuric acid required two hours of agitation at room temperature to form a homogeneous solution. The proton NMR spectrum of

* Aerojet-General Report 0235-01-18, January 1964, p. 4 (Confidential).

** Aerojet-General Report 0235-01-16, March 1963, pp. 4-5 (Confidential).

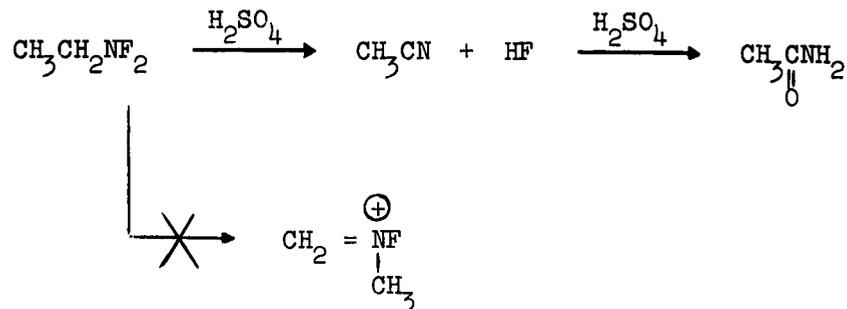
*** Aerojet-General Report 2730, October 1963, p. 12 (Confidential).

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II Technical Discussion, A (cont.)

Report No. 2945

this solution indicated a mixture of acetonitrile and acetamide; acetonitrile was found to undergo hydration in sulfuric acid to acetamide in several hours. There was no evidence of methyl migration to form an immonium ion:



The reaction of 1,1-dichloro-1-buten-3-one with difluoramine was previously shown to give either 3,3-bis(difluoramino)-1,1-dichloro-1-butene or N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide, depending on the experimental conditions.* Some further work was done to determine the chemical properties of these materials.** Thus, the hydration of 3,3-bis(difluoramino)-1,1-dichloro-1-butene would be expected to give a β,β-bis(difluoramino)carboxylic acid. No reaction took place when this olefin was heated with dilute sulfuric acid or with constant boiling hydrochloric acid. When the olefin was heated with concentrated sulfuric acid, it decomposed, and no product could be isolated. The olefin was also found to be unreactive toward bromine in carbon tetrachloride or water. The reaction of the olefin with alcoholic sodium hydroxide gave a material with acetylenic absorption in its infrared spectrum.

When N-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide was treated with aqueous sodium hydroxide, a homogeneous solution was formed. When this solution was acidified, a new compound precipitated, which was identified by elemental analysis and by infrared, proton, and fluorine NMR spectra as N-[2,2-dichloro-1-fluorimino-2-(difluoramino)ethyl]-acetamide. This material was found to be soluble in aqueous base and insoluble in acid. Its acidic properties are attributed to the amide hydrogen, the removal of which gives an anion stabilized by the carbonyl and fluorimino groups.

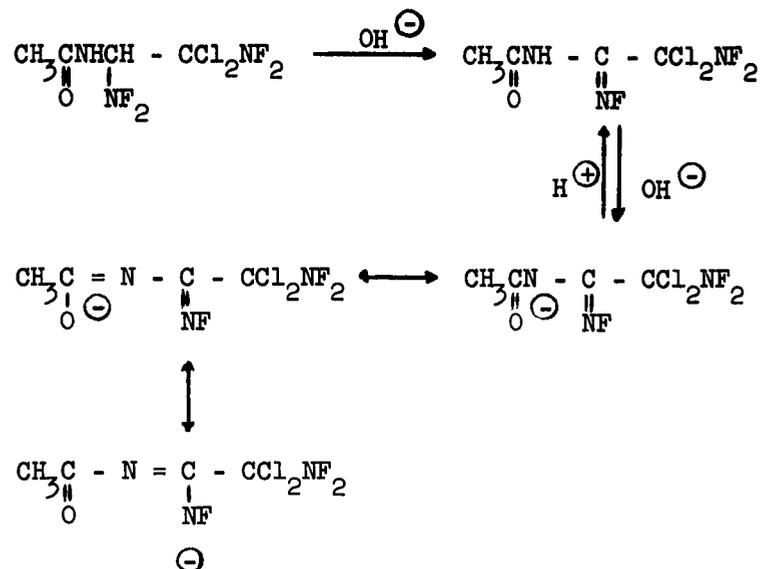
* Aerojet-General Report 2730, October 1963, p. 5 (Confidential).

** Aerojet-General Report 0235-01-18, January 1964, p. 2 (Confidential).

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II Technical Discussion, A (cont.)

Report No. 2945



3. Experimental

a. α -Bromo- α,α -bis(difluoramino)toluene

To a refluxing mixture of approximately 27 g of difluoramine and 12 ml of 20% fuming sulfuric acid was added dropwise, with stirring, 5.0 g (0.0170 moles) of α,α -dibromo- α -nitrotoluene.* After 4 hours, 50 ml of methylene chloride was added, and the mixture was stirred for 5 min. Unreacted difluoramine was removed, and the lower (sulfuric acid) layer was drained onto ice and was discarded. The methylene chloride layer was dried over sodium sulfate and was then distilled. After the methylene chloride was removed, vacuum distillation gave 3.35 g (0.0122 moles, 72% yield) of α -bromo- α,α -bis(difluoramino)toluene, b.p. 32°C/0.4 mm.

Anal. Calc'd for $\text{C}_7\text{H}_5\text{N}_2\text{F}_4\text{Br}$: C, 30.8; H, 1.83; N, 10.25; F, 27.8.

Found: C, 30.9; H, 1.84; N, 10.4; F, 28.3.

The infrared spectrum of α -bromo- α,α -bis(difluoramino)toluene is shown in Figure 1. The proton NMR spectrum (Figure 2) consists of a

*G. Ponzio, Gazz. chim. ital., 38 II, 418 (1908).

CONFIDENTIAL

II Technical Discussion, A (cont.)

Report No. 2945

complicated aromatic multiplet, with prominent absorptions at 450 cps and 465 cps (tetramethyl silane, TMS, standard). The fluorine spectrum (Figure 3) consists of an AB quartet, with chemical shifts of -42.17 and -45.04 ppm, and a coupling constant of 601 cps (CFCl_3 standard).

b. 1,1-Bis(difluoramino)-1-chloropropane

Redistilled 1-chloro-1-nitropropane (10.0 g, 0.081 mole) was added to a solution of 5.0 g (0.125 mole) of sodium hydroxide in 40 ml of water at 0 to 5°C. The mixture was kept at this temperature range and was stirred vigorously for 1.5 hours until a clear solution was formed. This solution was added dropwise to an Erlenmeyer flask containing a partially frozen nitrous acid solution that was prepared by slowly adding 8.6 g (0.122 mole) of sodium nitrite to a solution of 15 g of concentrated sulfuric acid in 100 ml of water. The flask was swirled while these reagents were added and the contents were kept partially frozen by intermittent cooling with a -80°C bath. A dark blue oil (7.6 g) separated, and was removed with a separatory funnel and was added to 25 g of pentane. The pentane solution was stored overnight at -80°C.

This pentane solution was added dropwise to a stirred refluxing mixture of approximately 27 g of difluoramine and 13 ml of 20% fuming sulfuric acid. After 4 hours, the mixture was added to 200 ml of ice. The pentane layer was separated and the aqueous layer was extracted with an additional 25 ml of pentane. The combined pentane layers were dried over sodium sulfate and distilled. After the solvent was removed, vacuum distillation yielded 0.2 g of colorless liquid, b.p. 31°C/60 mm. Gas chromatography, using a 1/4-in. column of 10% UCON 50HB100 on Teflon at 76°C with a helium flow rate of 60 ml/min, indicated that the liquid contained two components with retention times of 15 and 25 min, and areas of 60 and 38%, respectively. The former component was trapped and characterized.

Anal. Calcd for $\text{C}_3\text{H}_5\text{N}_2\text{F}_4\text{Cl}$: C, 20.3; H, 2.82; N, 15.8; F, 8.

Found: C, 20.4; H, 3.33; N, 16.1.

The infrared spectrum of 1-chloro-1,1-bis(difluoramino) propane is shown in Figure 4. The 60-mc proton NMR spectrum (Figure 5), using

CONFIDENTIAL

II Technical Discussion, A (cont.)

Report No. 2945

CCl_4 as the solvent and TMS as the reference, consists of a triplet at 1.26 ppm assigned to the methyl and a quartet of 2.45 ppm assigned to the methylene. The 56.4-mc fluorine spectrum (Figure 6), using CFCl_3 as reference, consists of an AB quartet, with chemical shifts of -29.94 and -36.91 ppm and a coupling constant of 611 cps.

c. Reaction of Ethyl Difluoramine with Sulfuric Acid

Ethyl difluoramine (0.1 ml) was condensed into a standard taper centrifuge tube and 1 ml of concentrated sulfuric acid was added. The stoppered tube was agitated for 2 hours with a vortex mixer until a clear homogeneous solution was formed. The proton NMR spectrum of this solution consisted of sharp singlets at 2.22 and 2.51 ppm and a weak broad band at 8.2 ppm. The band positions are referred to tetramethyl silane (TMS), using tetramethylammonium ion as the internal standard, with a correction of 3.10 ppm.* The signal at 2.22 ppm decreased with time and the other two signals increased. After 48 hours, the spectrum consisted of only a strong singlet at 2.52 ppm and a weak one at 8.2 ppm. The NMR spectrum of acetonitrile in concentrated sulfuric acid was identical to that of ethyl difluoramine, and underwent the same changes. After 2.5 hours the 2.22-ppm signal had disappeared almost completely. The NMR spectrum of acetamide in sulfuric acid consisted of a sharp singlet at 2.51 ± 0.2 ppm and a broad weak signal at 8.3 ± 0.2 ppm.

B. DIRECT FLUORINATION (V. Grakauskas)

1. General Remarks

From the beginning of this program, practically all direct fluorination work has been done in aqueous solutions. In most cases these reaction conditions were satisfactory and the desired NF compounds were obtained in relatively good yields. This has been particularly true with simple nitrogenous substrates. However, difficulties were encountered when attempts have been made to expend this fluorination study to more complex compounds. In some cases such substrates were completely insoluble in water and did not react with fluorine at all, in other cases it appeared that intermediates leading to more complex NF

*N. Deno, et. al., J. Am. Chem. Soc., 85, 2991 (1963).

CONFIDENTIAL

II Technical Discussion, B (cont.)

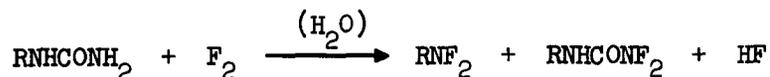
Report No. 2945

compositions were decomposed by water. To overcome these difficulties, from time to time, other solvents were investigated, but with only limited success until recently. In the middle of this contract year it was found that simple aliphatic esters and nitriles are very useful solvents in which to carry out the direct fluorination of a variety of nitrogenous substrates. At about the same time, it was also found that many liquid nitrogenous compounds could be selectively fluorinated on nitrogen in the absence of a solvent. These new fluorination conditions were exploited during the last two quarters, using simple amides and carbamates as model compounds. The results of this work indicated that in many cases the yield of NF compounds obtained under these fluorination conditions were significantly higher than those obtained in analogous fluorination in aqueous solution. It now appears that more complex nitrogenous substrates might undergo fluorination under these reaction conditions leading to more sophisticated products than could be obtained by working in aqueous solutions.

2. Discussion

a. Ureas

In the early work, it was found that the fluorination of aqueous monoalkyl ureas gives the corresponding alkyldifluoramines and N,N-difluoro-N'-alkyl ureas:*



More recently, the fluorination of aqueous n-propylurea has been studied on a larger scale, and in addition to N,N-difluoro-N'-n-propylurea and n-propyldifluoramine, N-fluoro-N-n-propylurea, $\text{C}_3\text{H}_7\text{NFCONH}_2$, has been also isolated from the fluorination mixture.**

The isolation of a new compound in the alkylurea series suggested that the fluorination of urea itself should be examined in a greater

* Aerojet-General Report No. 2099, November 1961, p. 17 ff (Confidential).

** Aerojet-General Report No. 0235-01-19, April 1964, p. 8 (Confidential).

CONFIDENTIAL

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

detail in an attempt to isolate, in addition to the previously identified N,N-difluorourea, other four possible reaction products:



The fluorination of aqueous urea has been reinvestigated with the primary objective of synthesizing monofluorourea.* Initial attempts to isolate the compound from the fluorination mixture (1:1 molar ratio of fluorine to urea) failed because of high solubility of fluorourea in water. However, spectroscopic evidence (F^{19} NMR spectrum) was obtained for the presence of fluorourea in the solution. The concentration of urea solution subjected to the fluorination was increased from 8-10% to 30 to 40% to obtain more concentrated solutions of fluorourea. At these higher concentrations, the fluorination still proceeded very smoothly and batches amounting to 4 moles of urea could be fluorinated in a matter of 1 to 1.5 hours. A mixture of N-fluoro- and N,N-difluorourea was extracted from the aqueous solution with diethyl ether and the compounds were separated by crystallization from methylene chloride, in which N-fluorourea is sparingly soluble, while N,N-difluorourea remained in solution.

Some of physical properties and chemical reactions of fluorourea are presented below.

Fluorourea is a white, nonhygroscopic solid, m.p. 56 to 57°C. The compound has been stored at 0°C for several months without noticeable decomposition. When stored at room temperature, fluorourea gradually turns yellow; the resulting yellow solid was identified as azodicarbonydiamide, $\text{NH}_2\text{CON}=\text{NCONH}_2$. Aqueous solutions of fluorourea can also be stored for several weeks at 0°C; at room temperature, however, azodicarbonydiamide gradually deposits. In the presence of urea, aqueous fluorourea decomposes at room temperature, resulting in the formation of biurea instead of azodicarbonydiamide. Fluorourea is very soluble in ethers, alcohols, and concentrated acids but is only sparingly soluble in alkanes and halocarbons.

*Ibid., p. 9 ff.

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

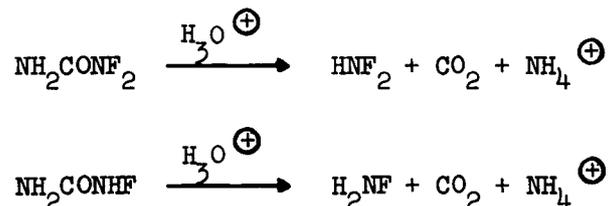
The impact sensitivity of fluorourea was determined with a Bureau of Mines tester and a 2-kg weight; with this machine, RDX on the bare anvil exhibits 50% firings at a 30-cm drop distance. The following values, in 2-kg-weight drop distance for 50% firings, were obtained from monofluorourea:

<u>Surface</u>	<u>Drop Distance, cm</u>
Bare anvil	34
Grit paper	30
Glass-fiber cloth	17

Differential thermal analysis shows that fluorourea exhibits an exotherm at 128°C.

The fluorourea needed for further study was made in batches of up to 45 g and 20% yield. No attempts were made to maximize the yield; N,N-difluorourea was obtained as a byproduct in all preparations.

It was thought that fluorourea might be a useful starting material for the preparation of fluoramine, just as N,N-difluorourea is used to generate difluoramine:



Numerous reactions of fluorourea have been investigated but, so far, all attempts to generate fluoramine have failed. These investigations are discussed below.

A solution of fluorourea in 50% sulfuric acid was warmed to 60°C, simulating conditions used in generating difluoramine from difluorourea. The reaction was complete in 1 hour, as evidenced by carbon dioxide evolution, but no NF compound was evolved. On dilution of the reaction mixture with ethanol, ammonium sulfite precipitated. It appears that fluorourea underwent hydrolysis as anticipated:

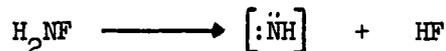


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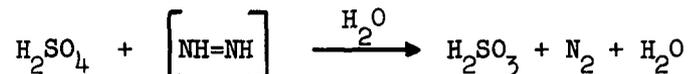
II Technical Discussion, B (cont.)

Report No. 2945

Fluoramine apparently decomposed under these conditions:



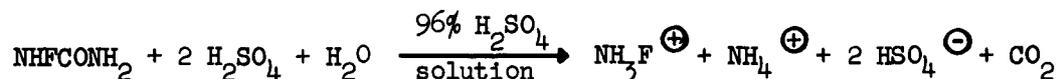
and the resulting imine (or diimine) reduced sulfuric acid to sulfite:



In summary, the overall reaction in 50% aqueous sulfuric acid can be represented as follows:

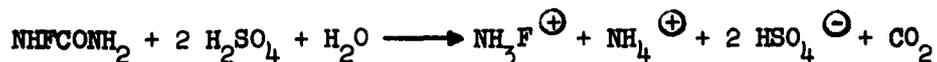


A dilute solution of fluorourea in 96% concentrated sulfuric acid was warmed to 40 to 50°C. Carbon dioxide was liberated at a rapid rate, and the reaction was complete in 15 min. The sulfuric acid solution contained N-fluoro-ammonium cation, as shown by its fluorine NMR spectrum. Upon dilution with tetrahydrofuran, an equimolar mixture of fluoroammonium bisulfate and ammonium bisulfate was obtained in the form of a white crystalline solid, in accordance with the following reaction:



Using only enough 96% sulfuric acid to conform with the stoichiometry of the above reaction, * some carbon dioxide but no NF compounds was evolved, and the reaction mixture solidified after 30 min at 30 to 35°C. The major products were hydrazine sulfate and ammonium sulfate. The change in the course of the reaction appears to be due to lack of sufficient water for hydrolysis to occur.

* Actual amounts of reagents used were 4.0 g of 96% sulfuric acid (~0.04 mole) and 1.6 g (0.02 mole) of fluorourea. This amount of sulfuric acid contains only 0.16 g (0.009 mole) of water, insufficient for the following reaction:



CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

Finally, fluorourea was hydrolyzed in 93% sulfuric acid using a 2.5-to-1 molar ratio of sulfuric acid to fluorourea and 1-to-1 molar ratio of water to fluorourea. A white solid identified as an equimolar mixture of fluoroammonium bisulfate and ammonium bisulfate precipitated upon dilution of the reaction mixture with tetrahydrofuran.

Alcoholysis of fluorourea was studied as another approach to the preparation of fluoramine. It was hoped that the reaction would follow the first of the two potential courses indicated below.



or



A solution of fluorourea in ethanol was refluxed for several hours. A small amount of azodicarbonydiamide, $\text{NH}_2\text{CON}=\text{NCONH}_2$, was produced instead of the expected products, and most of the fluorourea was recovered unchanged. Turning to a higher-boiling alcohol and more vigorous reaction conditions, biurea was obtained when a solution of fluorourea in ethylene glycol was heated. Apparently, some of the fluorourea oxidized glycol and, in turn, was reduced to urea; this urea then coupled with fluorourea, producing biurea.

Fluorourea dissolved in acetic anhydride at room temperature without apparent reaction. Cyanuric acid was formed when this solution was heated to 65 to 70°C.

In the presence of concentrated sulfuric acid, fluorourea reacts with aldehydes and ketones, producing nitriles and amides, respectively:



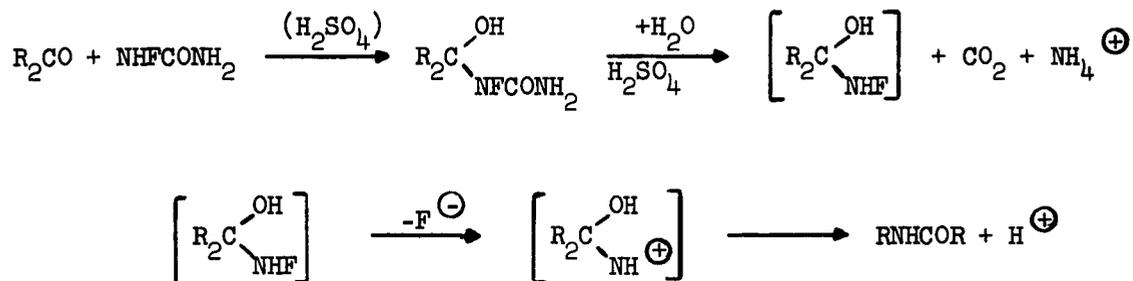
The reaction is rapid and complete; a solution of fluorourea in 3-pentanone was "titrated" with concentrated sulfuric acid until the evolution of carbon dioxide

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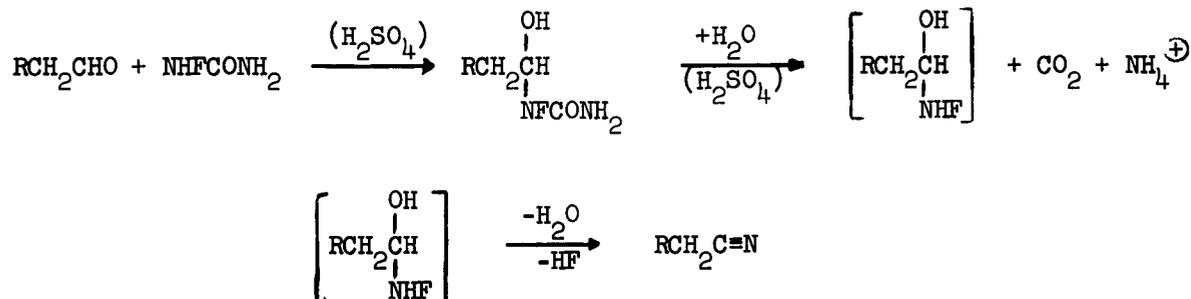
II Technical Discussion, B (cont.)

Report No. 2945

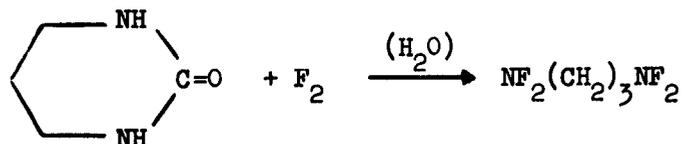
ceased. After removal of ammonium bisulfate and excess ketone, N-ethylpropionamide was obtained in almost quantitative yield. Since fluorourea reacts slowly with concentrated sulfuric acid at room temperature, and does not react at all with ketones in the absence of an acid, it seems that reaction with ketones involves the formation of a 1-to-1 adduct, which in turn undergoes hydrolysis and re-arrangement as shown below.



A similar consideration applies to the reaction of fluorourea with aldehydes:



The fluorination of aqueous tetrahydro-2-pyrimidone (trimethyleneurea) was studied with the objective of obtaining an improved method for the preparation of 1,3-bis(difluoramino)propane: *



However, only a 5 to 7% yield of this product was isolated from the reaction mixture. The main reaction product was identified as 3-difluoramino-propylcarbonyl

* Aerojet-General Report No. 0235-01-18, January 1964, p. 8 ff (Confidential).

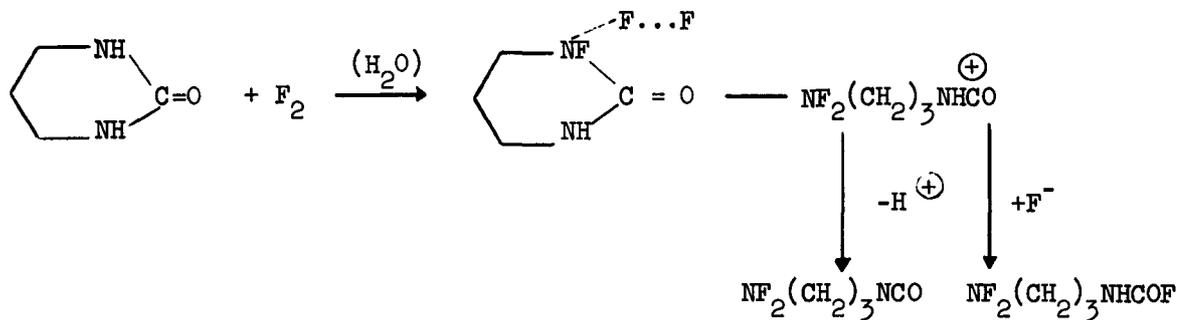
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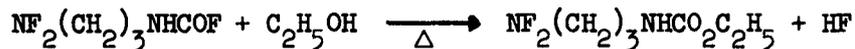
Report No. 2945

fluoride, $\text{NF}_2(\text{CH}_2)_3\text{NHCOF}$. Other products of this reaction were 3-difluoroamino-propyl isocyanate, $\text{NF}_2(\text{CH}_2)_3\text{NCO}$ and 3-difluoraminoacetonitrile, $\text{NF}_2(\text{CH}_2)_2\text{CN}$. The latter apparently resulted from the dehydrofluorination of 1,3-bis(difluoro-amino)propane.

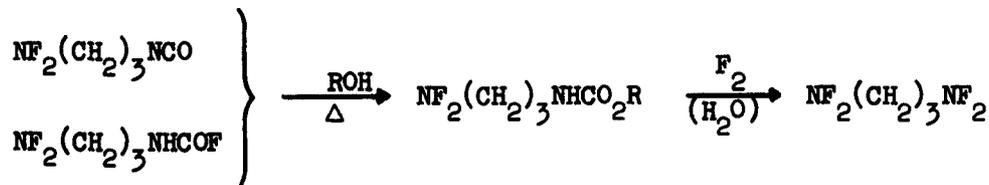
An acylium ion seems to be the common intermediate for the formation of both the carbamyl fluoride and the isocyanate:



3-Difluoraminoacetonitrile and 3-difluoroamino-propyl isocyanate apparently did not react with water during the fluorination because of their insolubility. The isocyanate reacted readily with alcohols to give the corresponding carbamates. The carbamyl fluoride, on the other hand, reacted very slowly, the reaction with ethanol proceeding only to 50% completion at room temperature in 5 days. When an ethanolic solution of 3-difluoroamino-propylcarbamyl fluoride was refluxed for 5 hours, ethyl 3-difluoroamino-propylcarbamate was obtained practically quantitatively:



Since the carbamyl fluoride and the isocyanate both react with an alcohol to give the same 3-difluoroamino-propylcarbamate, the crude fluorination mixture of trimethyleneurea can be readily converted to the compound. The carbamate, in turn, was expected to produce 1,3-bis(difluoroamino)propane on fluorination:



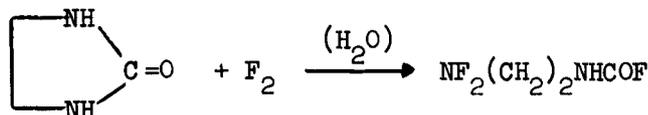
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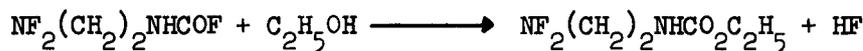
Report No. 2945

This possibility was investigated, but it was only partially successful due to the low yield in the fluorination step.

The fluorination of aqueous 2-imidazolidone (dimethylene-urea) was also investigated* and the reaction followed a course similar to that of tetrahydro-2-pyrimidone. The major product of the reaction was identified as 2-difluoraminoethyl-carbamyl fluoride:



The material was converted to the corresponding carbamate by reaction with ethanol:

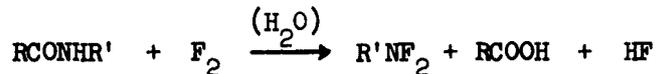


b. Amides

It has been previously shown that the fluorination of primary amides in aqueous solution results in the formation of the corresponding amines,** and the reaction has been rationalized by the formation of N-fluoroamides, followed by the Hofmann rearrangement:



The fluorination of aqueous monoalkylamides, on the other hand, gave the corresponding alkyl difluoramines:***



* Aerojet-General Report No. 0235-01-19, April 1964, p. 14 (Confidential).

** Aerojet-General Report No. 2730, p. 23 (Confidential).

*** Aerojet-General Report No. 2099, November 1961, p. 21 (Confidential).

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

The presence of N-alkyl-N-fluoroamide intermediates in these reactions has been suggested,* but the intermediates have not been isolated. The fluorination of amides has been studied more thoroughly during the past year with the objective of synthesizing N-monofluoro derivatives, which appeared to be useful intermediates.

The possibility of synthesizing N-fluoroformamide itself, HCONHF, was investigated first** because of the potential utility of the compound as an intermediate for the preparation of fluoroammonium perchlorate:



It has already been shown that the fluorination of aqueous formamide gives N,N-difluorourea*** and therefore, fluorination in aqueous solution did not appear promising; i.e., it seemed unlikely that a variation of reaction conditions would change the course of the reaction. Instead, pure formamide was fluorinated at 0 to 30°C. The fluorination proceeded smoothly and fluorine was readily consumed. A solid material gradually accumulated as the reaction progressed. This solid was removed by filtration at the end of the fluorination and identified as cyanuric acid. The clear filtrate on standing at 0 to 5°C gradually deposited more cyanuric acid. The rate of the formation of cyanuric acid increased significantly when an aliquot of the fluorination mixture was allowed to warm to room temperature. Another aliquot of the mixture was examined by NMR; the F¹⁹ NMR spectrum indicated the presence of hydrogen fluoride and a doublet at -65.91 ppm suggesting -NHF structure. This doublet signal was tentatively assigned to N-fluoroformamide. When the solution in the NMR sample tube warmed to 25 to 28°C, the intensity of the doublet signal gradually weakened and cyanuric acid deposited. On the basis of the above observations, it is concluded that formamide undergoes fluorination giving relatively unstable fluoroformamide, which then gradually decomposes to cyanuric acid:

* Ibid., p. 22

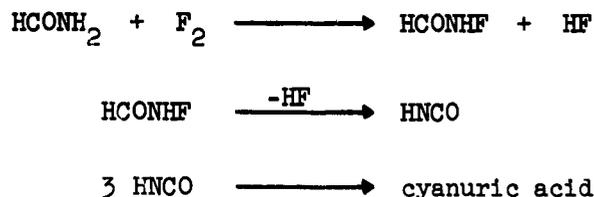
** Aerojet-General Report 0235-01-20, July 1964, p. 7 ff.

*** Aerojet-General Report 2730, October 1963, p. 24 (Confidential).

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945



When the formation of fluoroformamide had been tentatively established, attempts were made to fluorinate formamide in the presence of perchloric acid with the objective of hydrolyzing fluoroformamide to fluoroammonium perchlorate in situ. These attempts, however, were unsuccessful. When the fluorination was carried out in an excess of perchloric acid, fluorine passed through the reaction mixture without reacting. When the ratio of the reagents was reversed, i.e., a small amount of perchloric acid was added to formamide, the fluorination proceeded in the same manner as with pure formamide. At the end of the run, the fluorination mixture contained fluoroformamide but no fluoroammonium salt, as determined by its F^{19} NMR spectrum. Thus, in this case perchloric acid did not interfere with the fluorination of formamide, but also did not hydrolyze fluoroformamide.

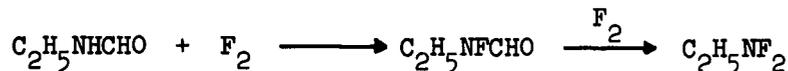
The fluorination of formamide, presently under further investigation, supplied several important general clues concerning the fluorination of nitrogenous organic compounds. First of all, it became evident that even in the absence of an inert solvent, nitrogenous organic compounds can be selectively fluorinated with elementary fluorine instead of being "burned" to CF_4 . It also suggested that in a solventless system organic nitrogenous compounds with long hydrocarbon chains might also undergo selective direct fluorination on nitrogen instead of an uncontrollable attack on the hydrocarbon portion of the molecule. These suppositions were found to be correct, as shown later in the discussion.

When the fluorination of formamide provided evidence that N-fluoroamide derivatives can be synthesized, the fluorination of monoalkylamides was investigated with the expectation that their N-fluoro derivatives might be less sensitive to decomposition, and thus possibly could be isolated and characterized. The fluorination of aqueous ethylformamide was studied next:

CONFIDENTIAL

II Technical Discussion, B (cont.)

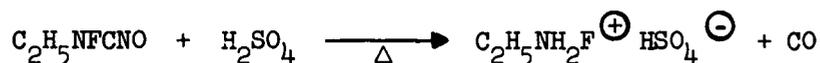
Report No. 2945



A volatile liquid was isolated from the fluorination mixture and the compound was identified as N-fluoro-N-formylethylamine.* The yield of the material was only 5%. A considerable amount of ethyldifluoramine was also produced in this fluorination, suggesting that under these reaction conditions N-fluoro-N-formylethylamine undergoes fluorination at a rate comparable with that of the starting material.

The fluorination of ethylformamide in the absence of a solvent was investigated next. The fluorination was carried out at -40 to -45°C and the reaction was accompanied by frequent localized fires in the reaction flask; fluorine, however, was readily consumed. At the end of the run, the reaction mixture was fractionated to remove, first, a mixture of hydrogen fluoride and ethyldifluoramine, and then N-fluoro-N-formylethylamine. The yield of the latter amounted to 50%, a significant improvement over the aqueous fluorination. Owing to the proximity of the boiling points of hydrogen fluoride and ethyldifluoramine, the mixture was not separated and the yield of ethyldifluoramine was not established.

N-Fluoro-N-formylethylamine was converted to N-fluoroethylammonium bisulfate by reacting it with an excess of concentrated sulfuric acid:**



The reaction was slow at room temperature, but was carried to completion in 45 to 60 min at 65 to 70°C. No attempts were made to isolate the pure salt. Its presence in sulfuric acid solution was confirmed by proton and fluorine NMR spectra. The slow hydrolysis of N-fluoro-N-formylethylamine is in agreement with the observed stability of fluoroformamide in formamide-perchloric acid solution at 0 to 3°C.

* Aerojet-General Report 0235-01-20, July 1964, p. 8 (Confidential).

** Aerojet-General Report 0235-01-20, July 1964, p. 9 (Confidential).

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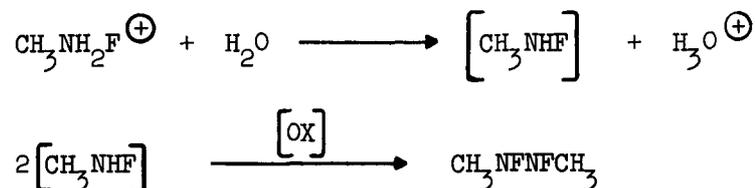
II Technical Discussion, B (cont.)

Report No. 2945

The fluorination of methylformamide (no solvent) was investigated next. The reaction was analogous to that of the ethyl derivative, except that fewer localized fires occurred. N-Fluoro-N-formylmethylamine was identified on the basis of its elemental analysis, its infrared spectrum, and its proton and fluorine NMR spectra.

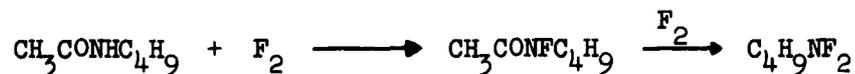
Similarly to the corresponding ethyl derivative, N-fluoro-N-formylmethylamine reacted with concentrated sulfuric acid to give N-fluoro-methylammonium bisulfate, $\text{CH}_3\text{NH}_2\text{F}^{\oplus}\text{HSO}_4^{\ominus}$, identified in sulfuric acid solution by its proton and fluorine NMR spectra.

One unsuccessful attempt was made to generate N-fluoro-methylamine in situ from its salt and oxidatively couple it to N,N'-difluoro-N,N'-dimethyl-hydrazine:



If it proceeded, this reaction would be analogous to the preparation of tetra-fluorohydrazine from difluoramine. Aqueous ferric ammonium sulfate was chosen as the oxidizing agent. The desired product was not obtained, and due to the small-scale experiment no other reaction products could be identified. Little emphasis should be placed on this sole "test-tube" experiment. The results simply mean that the desired hydrazine derivative was not obtained under these reaction conditions. In the absence of additional experimental work at this time, the reaction is presented here as a possibility that others may wish to investigate.

To extend the scope of amide fluorination reactions, aqueous n-butylacetamide was fluorinated:



No attempt was made to isolate butyldifluoramine. A small amount of a higher-boiling product was isolated and the material was identified as N-acetyl-N-fluoro-n-butylamine.

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

Fluorination in the absence of a solvent was extended to a cyclic amide, 2-pyrrolidinone.* Two products were isolated: N-fluoro-2-pyrrolidinone, previously obtained in the aqueous fluorination of 2-pyrrolidinone,** and 3-difluoramino-butyl fluoride:**



Due to the high freezing point of 2-pyrrolidinone, the fluorination in this case was started at 25-27°C and the reaction temperature was gradually lowered to 5-7°C as the concentration of the reaction products in the solution increased, and lowered the freezing point of the starting material. The fluorination was accompanied by frequent localized fires at the tip of the gas-inlet tube, producing some carbonaceous material.

In related work, the fluorination of aqueous 2-oxazolidone was investigated. In this case both N-fluoro-2-oxazolidone and 2-difluoramino-ethanol*** were obtained:



The main objective was to synthesize N-fluoro-2-oxazolidone and, therefore, the fluorination was stopped at a 1:1 molar ratio of fluorine to substrate. From the results it appears that at a 2:1 molar ratio of the reagents, this method would be a better and simpler route to 2-difluoraminoethanol than the previously reported two-step synthesis starting with N-2-hydroxyethylamides.****

In a continuing search for useful solvents that will withstand fluorine, dimethylformamide was considered as a good ionizing medium,

* Aerojet-General Report 0235-01-20, July 1964, p. 10-11 (Confidential).

** Aerojet-General Report 0235-01-15, January 1963, p. 13 (Confidential).

*** Aerojet-General Report 2730, October 1963, p. 25 (Confidential).

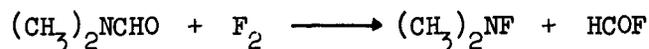
**** Ibid.

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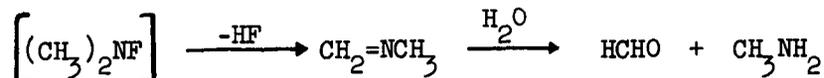
II Technical Discussion, B (cont.)

Report No. 2945

possessing good solubility characteristics, and probably inert to the action of fluorine, at least in the presence of reactive substrates. A control run was carried out and it was found that fluorine was readily consumed by dimethylformamide. There was very little firing at -40 to -50°C , and the resulting straw-yellow fluorination mixture oxidized potassium iodide. The solution retained the oxidizing properties for at least several days when stored at -80°C . However, when the mixture was allowed to warm to room temperature it gradually turned dark, gassed, and rapidly lost its oxidizing power. The oxidizing compound present in the solution has not yet been identified, but it may be dimethylfluoramine:



The compound apparently is unstable at ambient temperatures and decomposes with the elimination of hydrogen fluoride. This path of decomposition has been previously observed in the fluorination of aqueous dimethylformamide where methylamine was isolated:*



The results of the fluorination of simple amides in non-aqueous solution suggested that the more complex amides might also undergo fluorination under these conditions. The fluorination of 1,3-bis(formylamino)propane was investigated with the main objective to arrive at a better route to 1,3-bis(difluoramino)propane. The fluorination of aqueous 1,3-bis(formylamino)propane has been previously investigated,** but the yield of 1,3-bis(difluoramino)propane under these conditions amounted to only 3 to 5%. Contrary to the sluggish fluorination in aqueous solution, the fluorination of 1,3-bis(formylamino)propane in acetonitrile proceeded smoothly and resulted in the formation of 1,3-bis(difluoramino)propane in 40 to 50% yields. The yield figure is based on the results

* Aerojet-General Report 2099, November 1961, pp. 212-22 (Confidential).

** Aerojet-General Report 2730, October 1963, p. 28 (Confidential).

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

of only two runs, and it is possible that further improvements will be made in the future. In addition to the desired compound, higher-boiling (some non-distillable) NF intermediates were also obtained. Only 3-difluoramino-1-(N-fluoro-N-formylamino)propane, $\text{NF}_2(\text{CH}_2)_3\text{NFCHO}$, could be isolated from this high-boiling fraction; the compound was identified on the basis of its elemental analyses, and its infrared and NMR (Figure 7) spectra.

c. Carbamates

The main application of direct fluorination in non-aqueous solutions has been in the case of carbamates, where the earlier aqueous fluorination work has been completely "redone." The reason for this apparent repetition was the necessity of larger amounts of N-fluoro- and N,N-difluorocarbamates for the preparation of N-fluoroammonium salts and difluoramine, respectively. Furthermore, considerable amount of earlier work has been devoted to the study of the fluorination of simple carbamic acid esters in aqueous solution and a large amount of data has been accumulated, allowing a good comparison between aqueous and non-aqueous fluorination conditions. The results of this work, together with earlier experimental data on the fluorination of simple carbamic acid esters is presented in the appendix.

In addition to the study presented in the paper, the fluorination of methyl n-butylcarbamate in the absence of a solvent was investigated. The fluorination, carried at 0 to -10°C , proceeded smoothly and from the fluorination mixture both n-butyl difluoramine and methyl N-n-butyl-N-fluorocarbamate were isolated. N-Butyl difluoramine was identified on the basis of its elemental analysis, and its infrared and NMR spectra (Figure 8 and 9).

d. Miscellaneous

During the course of direct fluorination studies, other related problems arose leading to some observations that might be of interest to workers in the fluorine field. These observations, mainly related to the synthesis of intermediates, are summarized in this section.

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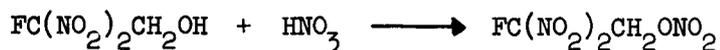
II Technical Discussion, B (cont.)

Report No. 2945

(1) Reactions of 2,2-Dinitro-2-fluoroethanol*

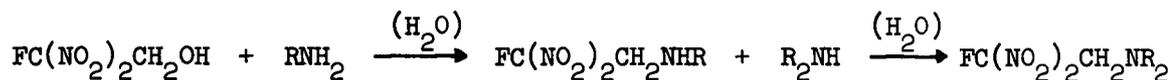
The oxidation of 2,2-dinitro-2-fluoroethanol was investigated with the objective of preparing 2,2-dinitro-2-fluoroacetaldehyde. This compound, if available, might be reacted with difluoramine to give energetic intermediates, and with nitroalcohols to give stable, lower-energy nitroplasticizers. In this connection, some other related reactions of 2,2-dinitro-2-fluoroethanol were also investigated.

Dinitrofluoroethanol reacted slowly with 100% nitric acid at room temperature to give the corresponding nitrate:



The somewhat impure compound was identified on the basis of its elemental analysis, and its infrared and NMR spectra. The alcohol also reacted slowly with 70% nitric acid, but the products have not yet been identified.

Dinitrofluoroethanol also reacted with primary or secondary amines to give the Mannich reaction products:



2,2-Dinitro-2-fluoroethylmethylamine ($\text{R} = \text{CH}_3$) was characterized on the basis of its elemental analysis, its infrared spectrum and its proton and fluorine NMR spectra. Similarly, 2,2-dinitro-2-fluoroethyldimethylamine was fully characterized. The hydrochloride salts of both amines were also prepared and characterized.

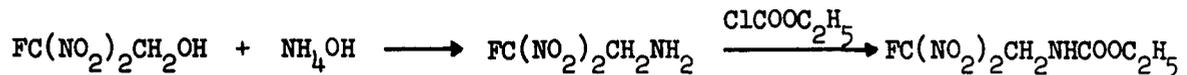
The reaction of dinitrofluoroethanol with an excess of concentrated ammonium hydroxide resulted in decomposition. On the other hand, a dilute aqueous solution containing an equimolar ratio of these reagents deposited a yellow water-insoluble liquid; this deposit exploded after it was isolated and was allowed to stand at room temperature overnight. In another experiment, the reaction product, in the original aqueous solution, was treated with an equimolar quantity of ethyl chloroformate:

*Aerojet-General O235-01-18, January 1964, p. 20 ff (confidential).

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

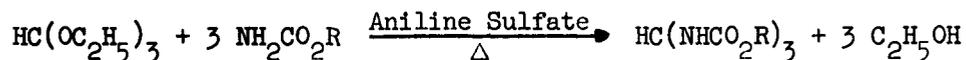


Ethyl 2,2-dinitro-2-fluoroethylcarbamate was obtained in 10 to 15% yields and was characterized on the basis of its elemental analysis, its infrared spectrum and its proton and fluorine NMR spectra. The main product of this reaction was 2,2-dinitro-2-fluoroethyl ethyl carbonate, $\text{C}_2\text{H}_5\text{OCOOCH}_2\text{C}(\text{NO}_2)_2\text{F}$. It is not clear why, if the reaction between the alcohol and ammonia was incomplete, chloroformate did not preferably react with ammonia. Methyl dinitrofluoroethylcarbamate was similarly synthesized from the crude amine and methyl chloroformate.

The possibility that dinitrofluoroethylcarbamates in the above reactions may be produced in a Mannich reaction between dinitrofluoroethanol and carbamate (produced from chloroformates and ammonia) was eliminated when it was shown in a separate experiment that an equimolar mixture of these reagents did not react, even at elevated temperatures.

(2) Reactions Between Orthoformates and Alkyl Carbamates*

Methanetriscarbamates, $\text{HC}(\text{NHCO}_2\text{R})_3$, which have not been reported previously, were synthesized in 45 to 50% yields by reacting ethyl orthoformate with alkylcarbamates at 110 to 150°C in the presence of a catalytic amount of aniline sulfate:



These compounds ($\text{R} = \text{CH}_3$ or C_2H_5) were characterized on the basis of their elemental analyses and their infrared spectra. The compounds were synthesized with the objective of using them as potential starting materials for the preparation of tris(difluoramino)-methane or partially fluorinated intermediates.

The fluorination of either trimethyl or triethyl methanetriscarbamate in aqueous suspension did not give the desired products.**

* Aerojet-General Report O235-01-18, January 1964, p. 10 (Confidential).

** Ibid., p. 11.

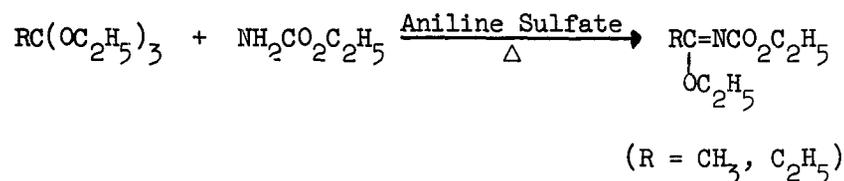
CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

Instead, a mixture of the corresponding alkylcarbamates and N-fluorocarbamates was isolated indicating the hydrolysis of either the starting materials or their N-fluoro derivatives.

Attempts also were made to synthesize 1,1,1-ethane- and 1,1,1-propanetriscarbamates from the corresponding orthoesters and alkylcarbamates. However, in both cases the reaction products were identified (elemental analysis, infrared and NMR spectra) as the corresponding N-carboalkoxyiminoethers:*



3. Experimental

a. Fluorination of 1,3-Bis(diformylamino)propane

1,3-Bis(diformylamino)propane, 130 g (1.0 mole), was fluorinated (without solvent) at 10 to 20°C until 35 liters of fluorine gas was consumed (6.5 hours). The fluorination was sluggish. Some unreacted fluorine passed through the reactor and localized firings occurred at higher fluorine flow rates. Attempts to work up the fluorination mixture by fractional distillation led to severe etchings of glass apparatus by hydrofluoric acid and (at higher temperatures) to partial decomposition of products. At this stage, the fractionation attempts were discontinued and the partially decomposed reaction mixture was added to 700 ml of water and the resulting mixture extracted with methylene chloride. The methylene chloride extracts were worked up to give 7 to 9 g of impure 1,3-bis(difluoramino)propane and 4 g of a colorless liquid (b.p. 31 to 32°C/0.2 to 0.3 mm, n_D^{25} 1.4035) which was found to be 1-(N-formyl-N-fluoroamino)-3-difluoramino)propane. An analytical sample was purified by gas chromatography.

Anal. Calc'd for C₉H₇N₂F₃O: C, 30.77; H, 4.52; N, 17.94; F, 36.51.
Found: C, 30.4; H, 4.6; N, 18.0; F, 36.6.

*Ibid.

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

The 60-mc proton (Figure 7) and 56.4-mc fluorine NMR spectra were obtained in carbontetrachloride solution with TMS and CFCl_3 added as internal references and employing the Varian microcell. The assignments are as follows:

H¹. The quintet at 2.14 ppm is assigned to the internal methylene group $-\text{CH}_2\text{CH}_2\text{CH}_2-$. The triplet (splitting 28.7 cps) of triplets at 3.61 ppm is assigned to the $\text{NF}_2\text{CH}_2\text{CH}_2$ -methylene group. This signal is overlapped by a doublet (splitting 32.6 cps) of triplets at 3.92 ppm which is assigned to the $-\text{CH}_2\text{CH}_2\text{NF}-$ methylene group. The doublet (splitting 11.3 cps) at 8.59 ppm is assigned to the aldehyde proton $-\text{NFCHO}$. The weak, broad signal at 7.95 ppm is attributed to impurities.

F¹⁹. The fluorine spectrum consists of a triplet (splitting 28 cps) at -54.6 ppm which is assigned to NF_2CH_2 - difluoramino group, and a broadened, poorly resolved triplet (splitting 32 cps) of doublets (splitting approximately 11 cps) at +79.1 ppm which is assigned to the $-\text{CH}_2\text{NFCHO}$ fluorine. The proton and fluorine spectra are consistent with each other and with the structure.

The fluorination of 1,3-bis(formylamino)propane in acetonitrile solution was used to prepare larger amounts of 1,3-bis(difluoramino)propane.

A solution of 195 g (1.5 mole) of 1,3-bis(formylamino)propane in 1500 ml of acetonitrile was fluorinated at -5°C until 140 liters (ca. 6 moles) of fluorine was consumed (3.5 hours). The reaction mixture was worked up remotely as follows. The fluorination mixture was added to 3500 ml of cold water and stirred vigorously for a few minutes. The phases were separated and the organic phase was washed with three 500 ml portions of cold water. The material was dried, filtered and fractionated to give 82 g (42% yield) of 1,3-bis(difluoramino)propane of 85 to 90% purity.

b. Fluorination of Methyl N-n-Butylcarbamate (No Solvent)

Methyl N-n-butylcarbamate, 131 g (1.0 mole), was fluorinated with elementary fluorine (diluted with nitrogen; 1:4) at 0 to -10°C , until 16

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

liters of fluorine was consumed (in 3.5 hours). The fluorination proceeded smoothly at low fluorine-nitrogen flow rates, but occasional localized fires occurred when attempts were made to speed up the reaction.

At the end of the run, a 50% aliquot of the reaction mixture was washed with three 100-ml portions of ice water. The organic layer was dried, filtered, and fractionated to give:

- (1) 10.6 g of a colorless liquid, b.p. 74°C
- (2) 13.0 g of a colorless liquid, b.p. 68 to $69^{\circ}\text{C}/25\text{ mm}$, n_D^{25} 1.4010
- (3) 17.0 g of starting material, b.p. 43 to $6^{\circ}\text{C}/0.1\text{ mm}$.

The material of fraction (1) was identified as n-butyldifluoramine:

Anal. Calc'd for $\text{C}_4\text{H}_9\text{NF}_2$: C, 44.03; H, 8.31; N, 12.83; F, 34.82.

Found: C, 44.3; H, 8.2; N, 12.8; F, 35.0.

The 60-mc proton (Figure 8) and 56.4-mc fluorine (Figure 9) NMR spectra were obtained using a carbon tetrachloride solution (TMS and CFCl_3 as internal references) in a Varian microcell. The assignments are as follows:

H'. The irregular triplet at 0.44 ppm is assigned to the terminal methyl group CH_3CH_2- . The triplet (splitting 28.9 cps) of triplets at 3.34 ppm is assigned to the methylene group adjacent to the nitrogen, $-\text{CH}_2\text{CH}_2\text{NF}_2$. The complicated multiplet with maximum intensity at 94 cps is assigned to the remaining methylene groups, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$.

F¹⁹. The fluorine spectrum consists of a single, broadened signal at -55.58 ppm, assigned to $-\text{CH}_2\text{NF}_2$ fluorine. The signal was too broadened to permit the determination of the coupling constant but the splitting appears to be the right order of magnitude.

The material of fraction (2) was identified as methyl N-n-butyl-N-fluorocarbamate.

Anal. Calc'd for $\text{C}_6\text{H}_{12}\text{NFO}_2$: C, 48.31; H, 8.11; N, 9.39; F, 12.74.

Found: C, 48.4; H, 8.5; N, 9.4; F, 12.6.

CONFIDENTIAL

II Technical Discussion, B (cont.)

Report No. 2945

The 60-mc proton and 56.4-mc fluorine NMR spectra were obtained using a carbon tetrachloride solution with TMS and CFCl_3 added as internal references. The assignments are as follows:

H¹. The irregular triplet of 0.96 is assigned to the terminal methyl of the $n\text{-C}_4\text{H}_9$ group, $\text{CH}_3\text{CH}_2\text{-}$. The complicated multiplet with maximum intensity of 93 cps is assigned to the two internal methylene groups, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$. The pair (splitting 34.7 cps) of triplets centered at 3.63 ppm is assigned to the methylene group adjacent to nitrogen $\text{-CH}_2\text{NF-}$. The intense signal at 3.79 ppm is assigned to the carbomethoxy methyl group, $\text{-CO}_2\text{CH}_3$.

F¹⁹. The fluorine NMR spectrum consists of a triplet (splitting 33.8 cps) at +70.92 ppm and is assigned to the $\text{-CH}_2\text{NFCO-}$ fluorine.

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

1. Introduction

The spectroscopic evidence for the formation of fluoroammonium ion in a reaction between alkyl N-fluorocarbamate and a mineral acid has been obtained two years ago.* Further work led to the isolation and characterization of fluoroammonium methanesulfonate salt.** The work of the last year has been directed towards preparation, isolation, and characterization of fluoroammonium perchlorate.

2. Discussion

The isolation of fluoroammonium methanesulfonate suggested that the perchlorate salt could also be synthesized. The reasons for the attempted synthesis of this salt are self-evident: the compound would be a potential solid oxidizer if its physical properties met the requirements, and if the increase in performance justified the cost of its production.

Both questions could be clarified by synthesizing the compound and determining its physical and chemical properties. In addition to these

* Aerojet-General Report 2381, October 1962, p. 32 (Confidential).

** Aerojet-General Report 2730, October 1963, p. 41 (Confidential).

CONFIDENTIAL

II Technical Discussion, C (cont.)

Report No. 2945

practical considerations, the fluoroammonium ion represents a novel type of NF bonding; the determination of physical-chemical properties of a salt would be useful for evaluation of further research in this area.

When the presence of fluoroammonium ion in the reaction mixture between isopropyl N-fluorocarbamate and 70% perchloric acid has been confirmed by F^{19} NMR spectrum, attempts to isolate the perchlorate salt have been initiated. The solution was concentrated at 10 microns in a molecular still and the residual crystalline solid was found to be the desired salt somewhat contaminated with perchloric acid.*

Because of the extended periods (40 hours) necessary to evaporate the solution to dryness, further attempts were made to isolate fluorammonium perchlorate from the slurry obtained by partial evaporation of the solution. The slurry was found to be soluble in diglyme, tetrahydrofuran, and ethyl acetate. Addition of ether, carbon tetrachloride or chloroform to the diglyme solution yielded oily products. However, washing of the slurry with dioxane left a crystalline material the analysis of which indicated a 1:1 complex of fluorammonium perchlorate and dioxane. This complex could also be isolated, in analytical purity, from a tetrahydrofuran solution of the slurry by precipitation with dioxane. Confirmation of the structure was obtained by F^{19} and proton NMR spectra.**

The fluorammonium perchlorate-dioxane complex was stable for several days in a dry atmosphere at room temperature. However, at 100°C, it decomposed rapidly.

Several attempts have been made to prepare fluoroammonium perchlorate by removing dioxane from the 1-to-1 fluoroammonium perchlorate-dioxane complex at reduced pressure. Thus, the dioxane content of the material was reduced to 4% by subjecting the complex to a pressure of 20 microns of Hg for 80 hours at room temperature. After an additional 60 hours under these conditions, carbon analysis showed no further loss of dioxane, although the analytical values for fluorine and nitrogen approached the theoretical values for fluoroammonium perchlorate. In another attempt to remove the last traces of dioxane, the temperature

* Aerojet-General Report 0235-01-18, p. 17, January 1964 (Confidential).

** Ibid.

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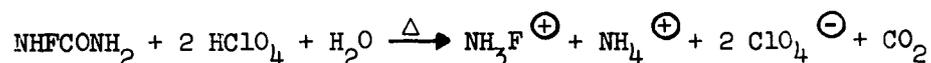
II Technical Discussion, C (cont.)

Report No. 2945

was increased to 40 to 45°C after the bulk of the dioxane was removed at room temperature. At 42 to 46°C and 20 microns, the residual material sublimed readily, coating the cooler portions of the apparatus with a white solid. Although the sublimate still contained 5.0% dioxane, the results suggested that fluoroammonium perchlorate itself could be sublimed. Work with the dioxane complex was halted at this point, and the purification of crude fluoroammonium perchlorate was resumed.

Crude fluoroammonium perchlorate solution, prepared by hydrolyzing isopropyl N-fluorocarbamate in 70% perchloric acid,* was concentrated under vacuum at room temperature. The resulting semisolid residue was sublimed at 45°C and 20 microns. A white crystalline solid collected on the walls of the apparatus just above the heated zone; it was identified as pure fluoroammonium perchlorate by means of elemental analysis. The pure material is extremely hygroscopic, necessitating the use of an explosion-proof dry box for the experimental work.

When fluorourea became available several attempts were made to use it as an alternate starting material in the synthesis of fluoroammonium perchlorate. Hydrolysis with 70% perchloric acid was expected to proceed as follows:



Carbon dioxide was evolved during the initial stages of the reaction, and the hydrolysis appeared to be proceeding smoothly. Rapid, uncontrolled reaction led to a "fume-off" after approximately one-third the theoretical amount of gas had been collected. A repetition of the reaction, using a more dilute solution of fluorourea in 70% perchloric acid, again terminated with a fume-off. By reducing the reaction temperature to 35°C, control was finally maintained while approximately two-thirds of the theoretical amount of gas was collected. Fluoroammonium perchlorate was not formed. The presence of nitrous oxide in the evolved gas suggests that decomposition of fluorourea occurred.

* Aerojet-General Report 2730, October 1963, p. 44.

CONFIDENTIAL

CONFIDENTIAL

II Technical Discussion, C (cont.)

Report No. 2945

The unsuccessful use of fluorourea led to the return of the preparation of fluoroammonium perchlorate from isopropyl N-fluorocarbamate and 72% perchloric acid. Several 30- to 50-mg batches of the compound were prepared following the sublimation procedure, with one small modification. The excess of perchloric acid was removed at 35 to 42°C, which significantly speeded up the concentration step. The material was used to determine its impact sensitivity. On the basis of a limited number of determinations, it was found that fluoroammonium perchlorate is not sensitive to impact (bare anvil, 2-kg weight) below 40 to 45 cm in a dry argon atmosphere; one positive firing occurred at 50 cm. To be certain that the salt did not become desensitized by the absorption of some moisture during the process of impact-sensitivity determination, a portion of the material was saved (same sample) and analyzed. Its elemental analysis (found: C, 0.35; H, 2.3; N, 10.0; F, 14.4) indicated that the salt was analytically pure; therefore, the impact-sensitivity data is valid.

Although the purification of fluoroammonium perchlorate by sublimation provided 50 to 100-mg batches of analytically pure material, the procedure is quite tedious and is not applicable for a large-scale operation. Therefore, during the last quarter attempts have been made to find a suitable solvent or solvent systems for crystallization of the salt. It was found that crude salt is very soluble in simple esters, such as methyl formate or acetate. Such solutions appear to be stable for at least several hours at room temperature.

When the ethyl acetate solution of crude fluoroammonium perchlorate was diluted with chloroform, a crystalline solid precipitated. Its nitrogen analysis suggested that the material is pure fluoroammonium perchlorate, but a complete elemental analysis is not yet available. If the additional analytical data confirmed the partial analysis, the purification of fluoroammonium perchlorate by crystallization would represent a significant improvement in its preparation technique.

3. Experimental

To 0.5 g (0.0043 mole) of isopropyl N-fluorocarbamate was added 2.0 ml of 70% perchloric acid and the reaction mixture was heated to 40-45°C over a 1-1/2 hour period. The solution was concentrated at 40-45°C/20 microns (Caution: volatile reaction products are hazardous) and the residual white solid

CONFIDENTIAL

CONFIDENTIAL

II Technical Discussion, C (cont.)

Report No. 2945

was treated under nitrogen with 1.0 ml ethyl acetate. A small amount of an insoluble material was removed by filtration under nitrogen and the clear filtrate was transferred to a dry box. Slow addition of chloroform to the solution caused the precipitation of a white crystalline solid, which was separated by filtration, washed with chloroform, and dried under vacuum.

Anal. Calc'd for FNH_3ClO_4 : N, 10.2.

Found: N, 9.78.

III. SUMMARY

A. REACTIONS OF DIFLUORAMINE

1,1-Dichloro-1-nitrobutane reacted with difluoramine in fuming sulfuric acid to give 1,1-dichloro-1-difluoramino-butane. 1,1-Dibromo-1-nitrobutane gave 1,1-dibromo-1-difluoramino-butane, which reacted further to give 1-bromo-1,1-bis(difluoramino)butane. α,α -Dibromo- α -nitrotoluene yielded α -bromo- α,α -bis(difluoramino)toluene. 1-Bromo-1,1-dinitrobutane did not react with difluoramine.

1-Chloro-1-nitrosocyclohexane and 1-nitro-1-nitrosocyclohexane reacted with difluoramine in sulfuric acid to give 1,1-bis(difluoramino)cyclohexane. 1-Nitro-1-nitrosocyclohexane and difluoramine in the presence of $\text{BF}_3 \cdot \text{H}_3\text{PO}_4$ gave nitrocyclohexane and 1-nitro-1-(fluoroazoxy)cyclohexane. 1-Chloro-1-nitro-1-nitrosoalkanes and difluoramine in fuming sulfuric acid gave 1-chloro-1,1-bis(difluoramino)alkanes. *n*-Octyl nitrite and *t*-butyl nitrite reacted with difluoramine to give the corresponding alcohols.

The reaction of *cis*-3-chlorocrotonic acid with difluoramine in sulfuric acid gave 3-chloro-3-difluoramino-butylric acid. 5-Nitro-2-pentanone yielded 5-nitro-2,2-bis(difluoramino)pentane.

The reaction of *t*-butyldifluoramine with boron trifluoride gave *N*-methyl-*N*-isopropylidene-*N*-fluoroammonium fluoborate. The reaction of ethyl difluoramine with sulfuric acid gave acetonitrile.

The reaction of *N*-[2,2-dichloro-1,2-bis(difluoramino)ethyl]acetamide with aqueous sodium hydroxide gave *N*-[2,2-dichloro-1-fluorimino-2-(difluoramino)ethyl]acetamide, which formed a stable anion.

CONFIDENTIAL

III Summary (cont.)

Report No. 2945

B. DIRECT FLUORINATION

The fluorination of aqueous urea at 1:1 molar ratio of fluorine to urea gave N,N-difluoro- and N-fluorourea. Some of the physical and chemical properties of fluorourea are described.

The corresponding ω -difluoraminoalkylcarbonyl fluorides were identified as the main reaction products in the fluorination of cyclic ureas.

N-Alkyl-N-fluoroamides were isolated in the fluorination of simple N-alkyl-amides. These compounds undergo hydrolysis with concentrated sulfuric acid to give the corresponding alkylfluoroammonium salts.

N-Fluoroformamide is the suspected reaction product in the fluorination of formamide in the absence of a solvent. The compound, however, readily decomposes with the formation of cyanuric acid.

The fluorination of 2-pyrrolidinone in the absence of a solvent gave its N-fluoro derivative and 3-difluoraminoethyl fluoride.

2-Difluoraminoethanol and N-fluoro-2-oxazolidinone were obtained in the fluorination of aqueous 2-oxazolidinone.

The work on the fluorination of simple carbamic acid esters, supplemented last year by additional data, is presented in a form of a complete paper.

The fluorination of methyl N-n-butylcarbamate in the absence of a solvent gave its N-fluoro derivative and n-butyl difluoramine in better yields than in aqueous fluorination.

Reactions of 2,2-dinitro-2-fluoroethanol with ammonia and amines gave Mannich reaction products.

Methanetriscarbamates and N-carboalkoxyiminoethers were synthesized by reacting orthoformates with alkyl carbamates.

C. FLUOROAMMONIUM SALTS

Fluoroammonium perchlorate was isolated from isopropyl N-fluoro-carbamate-70% perchloric acid hydrolysis mixture by sublimation. Several 50- to 100-mg batches of the compound were prepared in this manner, and both an elemental analysis and impact sensitivity were obtained.

Page 39

CONFIDENTIAL

CONFIDENTIAL

III Summary, C (cont.)

Report No. 2945

Fluoroammonium perchlorate-1,4-dioxane complex (1:1) was obtained by adding 1,4-dioxane to a diglyme solution of fluoroammonium perchlorate. Attempts to purify crude fluoroammonium perchlorate via the formation of its dioxane complex, followed by removal of dioxane under vacuum were unsuccessful.

Purification of fluoroammonium perchlorate by crystallization from ethyl acetate-chloroform seems to be promising, but complete analyses on re-crystallized product are not yet available.

IV. CONCLUSIONS AND RECOMMENDATIONS

A. REACTIONS OF DIFLUORAMINE

Chlorine, bromine, nitro, and nitroso groups were studied as leaving groups in difluoramine reactions under acidic conditions. 1-Nitro-1,1-dichloroalkanes and 1-nitro,1,1-dibromoalkanes readily undergo replacement of the nitro group by difluoramine. Replacement of a halogen in the products proceeds much more rapidly in the case of the bromine derivatives than in the case of the chlorine derivatives. The replacement of the halogen from a 1-halo-1,1-bis-(difluoramino)alkane has not yet been accomplished, although this reaction still appears to be feasible. Nitroso groups are also effective leaving groups in difluoramine reactions in sulfuric acid. N-Fluoroazoxy derivatives may be intermediates in this reaction. A nitro and a nitroso group on the same carbon atom can both be replaced by difluoramine. However, gem-dinitro compounds appear to be unreactive. Alkyl nitrites undergo N-O cleavage rather than C-O cleavage in liquid difluoramine.

The acid catalyzed rearrangement of t-alkyldifluoramines to immonium ions appears to be a general reaction. The n-alkyl derivatives, however, undergo HF elimination to form nitriles, at least in sulfuric acid.

A fluorimino group is capable of supporting a negative charge, as evidenced by N-[2,2-dichloro-1-fluorimino-2-(difluoramino)ethyl]acetamide.

B. DIRECT FLUORINATION

A general observation concerning the direct fluorination of nitrogenous compounds in solution made toward the end of this contract year was that

CONFIDENTIAL

IV Conclusions and Recommendations, B (cont.)

Report No. 2945

these reactions proceed more cleanly in organic solvents, such as acetonitrile or methyl formate, than in aqueous solution. It was also found that liquid carbamates and amides can be selectively fluorinated in the absence of a solvent. In some cases as high as ten-fold increase in yields resulted going from aqueous to non-aqueous fluorination. Work is now in progress in an attempt to understand the reasons for this pronounced "solvent effect" and to apply these fluorination conditions to more complex substrates. In addition to the advantages in our own work, it may be possible that fluorination in organic solvents (particularly in aliphatic nitriles) would be also advantageous for "fast-fluorination" of PFG adducts.

C. FLUORAMMONIUM SALTS

The work in this area has been concentrated on the preparation of fluoroammonium perchlorate. The compound has been synthesized and characterized. The purification by sublimation was ruled out as too tedious for larger-scale (1- to 10-g) operation and it became imperative to find a simpler alternative purification technique. This search is not yet completed, but on the basis of visual observations and fragmentary elemental analysis, it appears that the salt can be purified by crystallization from ethyl acetate-chloroform mixture. The purification of fluoroammonium perchlorate by crystallization would represent a significant improvement in its preparation techniques.

V. PERSONNEL

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

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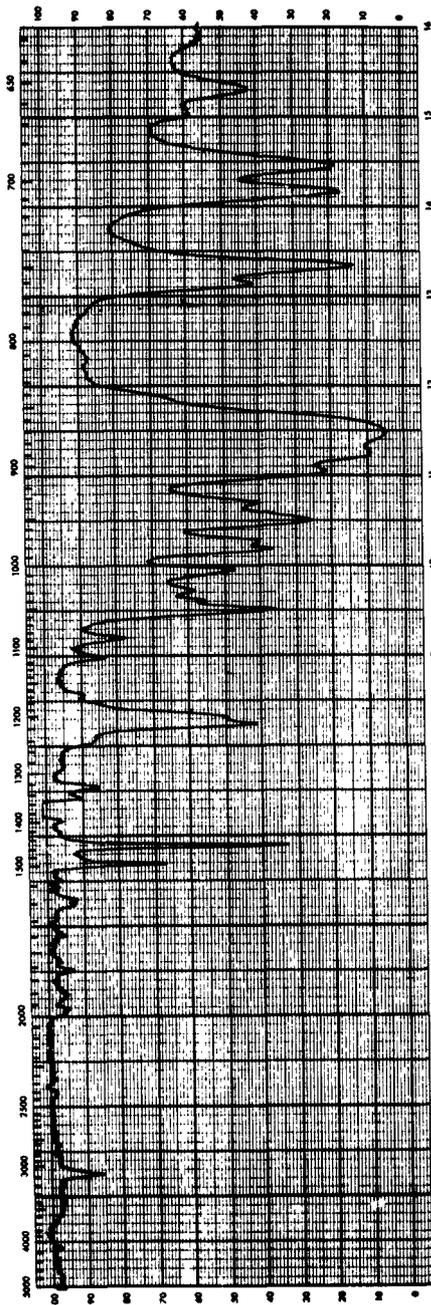


Fig. 1 Infrared Spectrum of α -bromo- α, α -bis(difluoramine)toluene

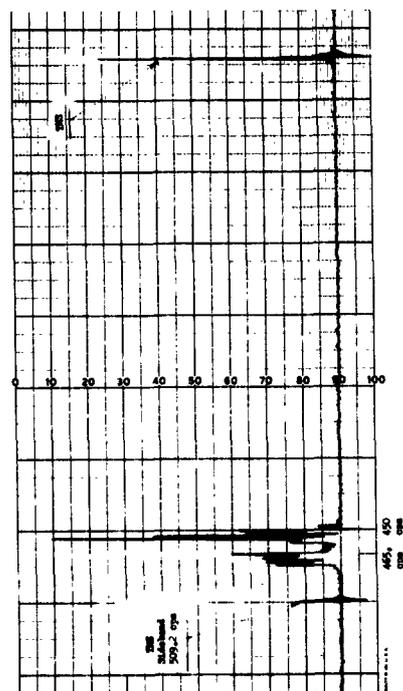


Fig. 2 Proton NMR Spectrum of α -bromo- α, α -bis(difluoramine)toluene

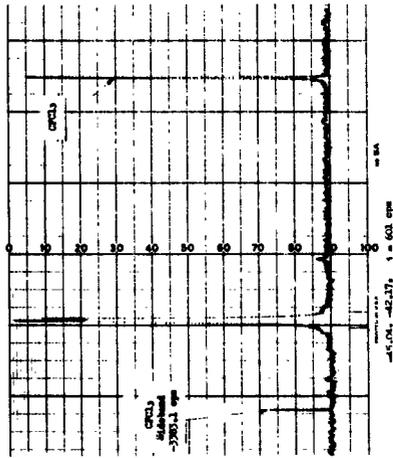


Fig. 3 Fluorine Spectrum of α -bromo- α , α -bis(difluoramino)toluene

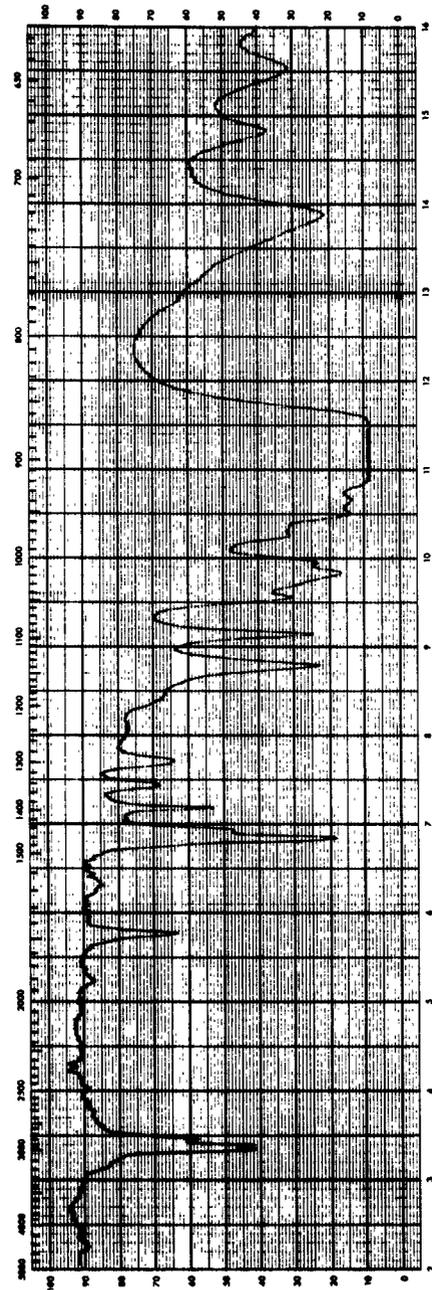


Fig. 4 Infrared Spectrum of 1-chloro-1,1-bis(difluoramino)propane

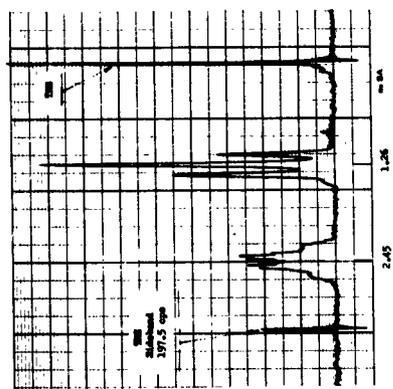


Fig. 5 Proton NMR Spectrum of 1-chloro-1,1-bis(difluoramino)propane

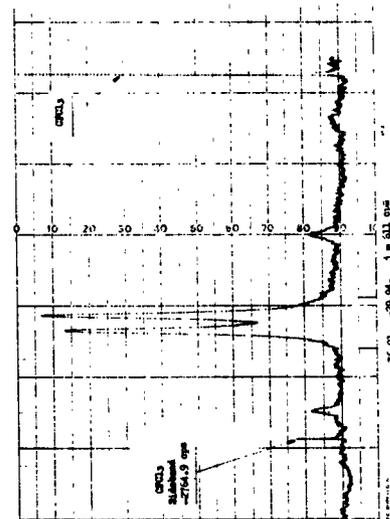


Fig. 6 Fluorine NMR Spectrum of 1-chloro-1,1-bis(difluoramino)propane

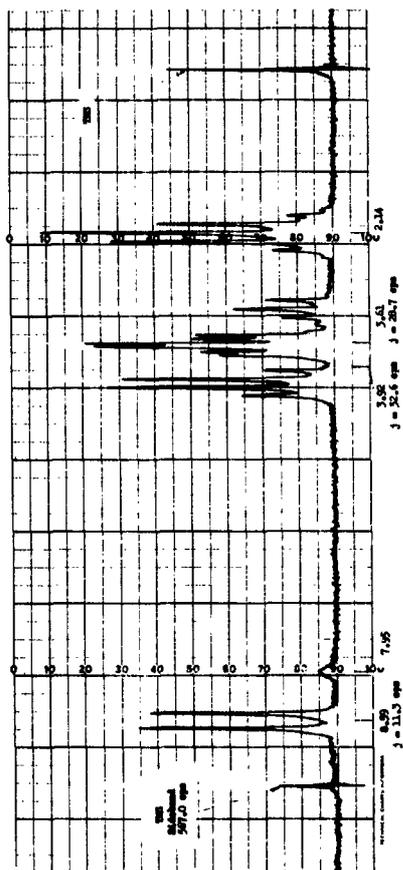


Fig. 7 Proton NMR Spectrum of 1-(N-fluoro-N-formylamino)-3-difluoraminopropane

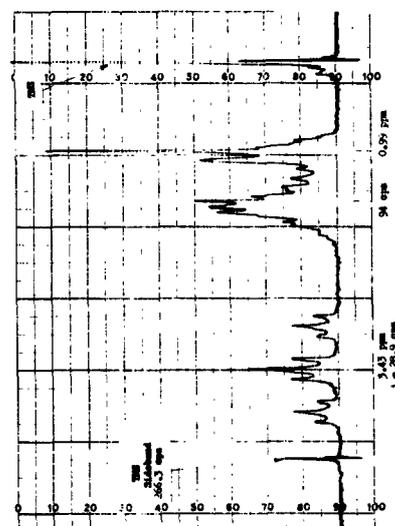
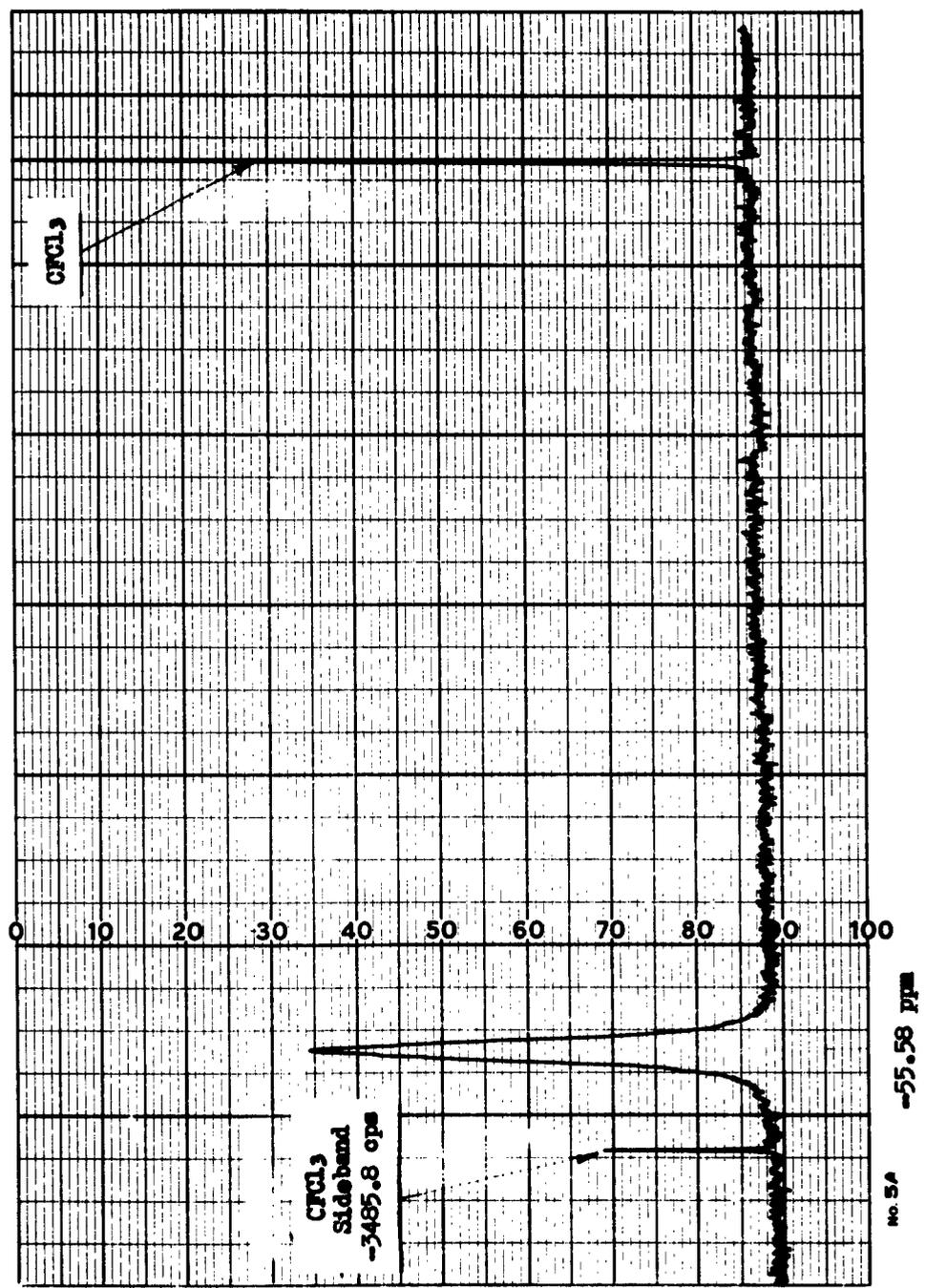


Fig. 8 Proton NMR Spectrum of n-Difluoraminobutane



Fluorine NMR Spectrum of n-Butyldifluoramine

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Report No. 2945

APPENDIX

DIRECT FLUORINATION OF ALKYL CARBAMATES IN SOLUTION

by

V. Grakauskas

(Contribution No. 262 from the Chemical Products
Division, Aerojet-General Corporation,
Von Karman Center, Azusa, California)

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Report No. 2945

ABSTRACT

N-Fluoro and N,N-difluoro derivatives of methyl, ethyl, isopropyl, and n-butyl carbamate were synthesized in 20 to 70% yields by direct fluorination of the corresponding carbamates in either aqueous solution or in organic solvents such as methyl formate or acetonitrile. Some reactions of these compounds have been investigated. Difluoramine was obtained quantitatively in the hydrolysis of N,N-difluorocarbamates with dilute mineral acids. The reaction of N,N-difluorocarbamate with aqueous sodium hypochlorite gave chlorodifluoramine. N-Fluorocarbamates dissolved in cold aqueous alkali, with the formation of relatively unstable alkali salts. Nucleophilic substitution reactions of sodium salt of ethyl N-fluorocarbamate with chlorine, bromine, ethyl chloroformate, and dimethyl sulfate have been examined.

Page A-11

CONFIDENTIAL

I. INTRODUCTION

The direct fluorination of carbamic acid esters in solution reported here represents a portion of a broader fluorination study which has been in progress in this laboratory for the past 7 years. One of the objectives of this study has been the synthesis of organic nitrogen-fluorine compounds and, for this purpose, a unique direct-fluorination technique has been developed. It has been found that certain nitrogenous organic compounds are selectively fluorinated on nitrogen when their solutions are subjected to the action of gaseous elementary fluorine. The hydrocarbon portion of the nitrogenous substrate molecule, including some functional groups, is not attacked by fluorine. The reactions have been carried out in aqueous solutions, as well as in a variety of organic solvents (e.g., methylene chloride, methyl formate, and acetonitrile). In all cases, these solvents were inert to the action of fluorine when nitrogenous substrates were present. Following this procedure, multi-mole batches of alkyl carbamates were fluorinated in a matter of hours, giving the desired N-fluoro derivatives in good yields. The reactions were carried out in all-glass apparatus, usually at temperatures of 0 to 5°C. The preparation of N,N-difluorourea by this technique has been already reported (Reference 1). The fluorination of alkyl carbamates discussed in this paper represents the continuation of the same study.

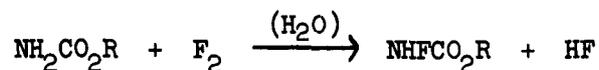
II. RESULTS AND DISCUSSION

Although mono- and disubstituted N-chloro and N-bromo derivatives of carbamic acid esters are known (Reference 2), the corresponding N-fluoro derivatives have not been reported. The successful fluorination of aqueous urea and the structural similarity between carbamic acid esters and urea, led to the investigation of the direct fluorination of carbamates. Initially, the fluorination has been studied in aqueous solution and under these reaction conditions

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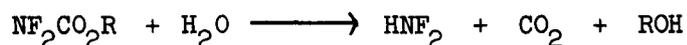
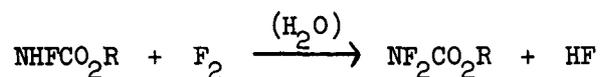
Report No. 2945

simple carbamic acid esters gave the corresponding N-fluoro derivatives in yields of 20 to 30%:



N-Fluoro derivatives of methyl, ethyl, isopropyl, and n-butyl carbamate were synthesized and the compounds were identified on the basis of their elemental analyses, their infrared spectra and their proton and fluorine NMR spectra. The analytical results and physical properties of these compounds are summarized in Tables A-1 and A-2.

A further examination of these fluorination reactions showed that, in addition to the N-fluoro derivatives, considerable amounts of difluoramine and carbon dioxide also are produced. The presence of these two additional reaction products suggested that N-fluorocarbamates undergo further fluorination to N,N-difluoro derivatives, which are unstable under reaction conditions and undergo hydrolysis:



To substantiate this supposition, the fluorination of carbamic acid esters in non-hydrolytic solvents has been investigated with the objective of isolating N,N-difluorocarbamates. Using acetonitrile or methyl formate as solvents, N,N-difluorocarbamates were obtained in 30 to 70% yields; in this manner, methyl, ethyl, isopropyl, and n-butyl N,N-difluorocarbamates were synthesized (see Tables A-3 and A-4 for the summary of their physical properties and analyses).

Although other esters and nitriles were found to be suitable solvents for these fluorinations, acetonitrile and methyl formate were found to be exceptionally useful because of their low boiling points. These solvents could be readily removed at the end of a fluorination, allowing an easy isolation of the

CONFIDENTIAL

Report No. 2945

reaction products. Using these relatively volatile solvents, fluorinations were carried out at temperatures of -40 to -50°C to prevent large losses of solvents by evaporation.

Because of the uncertainty in the fluorine measuring system, in some cases N,N-difluorocarbamates contained small amounts of starting materials, as well as some of the corresponding N-monofluoro derivatives. The difference in the boiling points of these components allowed the separation of the individual compounds by fractional distillation. In cases where the fluorine to substrate ratio was significantly lower than 2:1, relatively smaller amounts of N,N-difluorocarbamates and larger amounts of monofluoro derivatives were obtained. Also, under these conditions, larger amounts of starting material were recovered. No attempts have been made to establish the dependence between the distribution of reaction products (mono- and difluorocarbamates) and reaction conditions (for example, reaction temperature and nature of the solvent), although it seems reasonable to suspect that such variations should be noticeable.

Alkyl N,N-difluorocarbamates are readily hydrolyzed by dilute mineral acids to give difluoramine, carbon dioxide, and the corresponding alcohol. In this manner difluoramine can be generated quantitatively and, therefore, N,N-difluorocarbamates are useful as intermediates for the preparation of difluoramine as is N,N-difluorourea.

CAUTION

N,N-Difluorocarbamates should be handled with care. It is conceivable that, under prolonged storage, they can undergo a slow hydrolysis caused either by trace amounts of moisture or by impurities, resulting in a gradual accumulation of difluoramine in solution and also in a gas phase. Difluoramine, and even more so, its mixture with air, is known to be extremely explosive.

In addition to being useful intermediates for the generation of difluoramine, N,N-difluorocarbamates can also be used for the preparation of chlorodifluoramine.

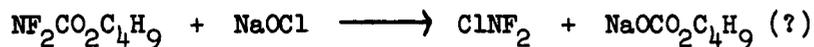
Page A-3

CONFIDENTIAL

CONFIDENTIAL

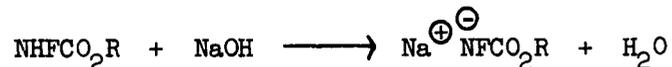
Report No. 2945

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



Alkyl N-fluorocarbamates represent a new class of organic nitrogen-fluorine compounds and some of their reactions have been investigated.

Alkyl N-fluorocarbamates have been stored without noticeable change at ambient temperatures for several years. The compounds dissolve readily in cold aqueous alkali to give a pale-yellow solution which is storable for several hours at 0 to 5°C. When allowed to warm to ambient temperatures, these solutions decomposed exothermically with the evolution of carbon dioxide and the formation of alkali fluorides. The decomposition pattern, however, seems to be more complex than these two simple decomposition products would suggest, and other unidentified organic decomposition products are also produced. The observation that N-fluorocarbamates cannot be extracted from their aqueous alkaline solutions suggests that the dissolution results in the formation of relatively unstable alkali salts of N-fluorocarbamates:



The fact that alkali salts of alkyl N-chlorocarbamates have been reported (Reference 3) substantiates this supposition.

When alkaline solutions of N-fluorocarbamates were acidified after a short period, N-fluorocarbamates were recovered by extraction of the aqueous solution with organic solvents.

The formation of alkali salts of alkyl N-fluorocarbamates apparently also resulted when the compounds were dissolved in alcoholic alkalies and alcoholic alkali alcoxides at subzero temperatures. Spontaneous, vigorous decompositions, accompanied by a strong exotherm and by gas evolution, occurred when such alkaline solutions were allowed to warm to ambient temperatures. Methyl ethyl iminodicarboxylic acid ester was identified as one of the decomposition products

Page A-4

CONFIDENTIAL

CONFIDENTIAL

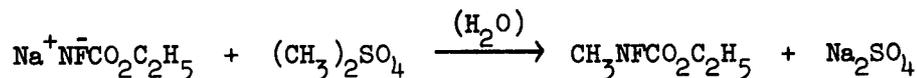
Report No. 2945

when ethyl N-fluorocarbamate solution in methanolic sodium methoxide was allowed to decompose in this manner. Similar decomposition in ethanolic sodium hydroxide yielded the corresponding diethyl ester.

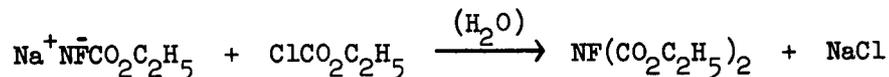
An aqueous solution of the sodium salt of ethyl N-fluorocarbamate has been halogenated with elementary chlorine and bromine to give the corresponding halo derivatives:



The methylation of sodium salt of ethyl N-fluorocarbamate with dimethylsulfate gave ethyl N-fluoro-N-methylcarbamate:

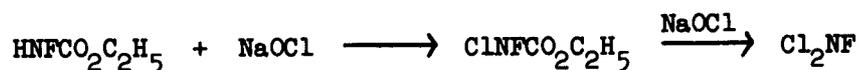


The salt also reacted readily with ethyl chloroformate to give diethyl fluoriminodicarboxylate:



It is interesting to note that the same fluoriminodicarboxylic acid ester has been subsequently identified as a side reaction product in the chlorination and bromination of aqueous sodium salt of ethyl N-fluorocarbamate, suggesting that ethyl chloro- and bromoformates are produced in those reactions.

The chlorination of ethyl N-fluorocarbamate has been also accomplished with stoichiometric quantities of aqueous sodium hypochlorite. However, when excessive amounts of hypochlorite were used, the reaction product was identified as dichlorofluoramine:



Dichlorofluoramine has been also obtained by either direct chlorination of ethyl N-fluorocarbamate in the presence of an excess amount of sodium hydroxide, or by reacting ethyl N-chloro-N-fluorocarbamate with aqueous sodium hypochlorite.

Page A-5

CONFIDENTIAL

CONFIDENTIAL

Report No. 2945

III. CONCLUSIONS

It is the opinion of the author that the main contribution of this study is not so much the synthesis of N-fluorocarbamates, but rather the generalizations that can be drawn from the experimental results. In conjunction with the fluorination of aqueous urea, the fluorination of carbamates further exemplifies the fact that a selective fluorination on nitrogen occurs when a solution of certain nitrogenous compounds in water or in organic solvents is subjected to the action of elementary fluorine. In the presence of such nitrogenous reaction sites, neither the solvent nor the hydrocarbon portion of the nitrogenous compound molecule is attacked by fluorine. The simplicity of the apparatus, the rapidity of the reaction, and high yields of products, seem to warrant the conclusion that the fluorination of carbamic acid esters is similar to their chlorination or bromination reactions.

IV. EXPERIMENTAL PROCEDURES

A. APPARATUS

A schematic drawing of the fluorination apparatus shown in Figure A-1 is self-explanatory. The amount of fluorine consumed in a fluorination experiment was determined volumetrically with the help of a calibrated auxiliary 500-ml stainless steel container (A). In large scale fluorinations, this container was recharged several times up to 350 psi from the main fluorine cylinder. A sodium fluoride tower (B) was placed in the fluorine line to remove traces of hydrogen fluoride and to preserve glass flowmeters from etching. Two identical glass flowmeters (D) were used to measure flow rates of nitrogen and fluorine. All gas lines up to the flowmeters were constructed of 1/4-in. stainless steel tubing. Gas lines below flowmeters were made of Pyrex glass tubing. Four-necked round-bottomed glass flasks, ranging in size from 100 ml to several liters, were used as the reactor (G). A mechanical stirrer (E), equipped with a glass Trubor stirring rod and glass or Teflon stirring blades, was used to agitate reactor contents. Glass inlet tubes and glass thermometers usually had to be replaced, after 20 to 40 runs, because of etching by hydrofluoric acid. Cold traps (H and I) were used to condense volatile reaction products when necessary. An

Page A-6

CONFIDENTIAL

CONFIDENTIAL

Report No. 2945

aqueous potassium iodide trap (J) served to indicate if unreacted fluorine and/or gaseous oxidizing products escaped from the reactor during the fluorination.

All glass ball-joints of the apparatus were greased with fluorine-resistant Kel-F grease. The stirrer shaft was lubricated with fluorocarbon oil. The whole system was flushed with nitrogen before a fluorination run. The nitrogen flow was then adjusted to a desired level and fluorine gas was admixed to the nitrogen stream at a desired concentration determined by flowmeter. The contents of the reactor were kept at a desired temperature either by ice water or by dry ice-trichloroethylene cooling baths. The whole operation was carried out behind shields. At the end of a run, the fluorine-gas valve was closed, and the system was flushed with nitrogen for 5 min.

B. REACTIONS

1. Alkyl N-Fluorocarbamates

The preparation of alkyl N-fluorocarbamates by the fluorination of aqueous alkyl carbamates is illustrated by two typical examples. All analytical data, as well as physical properties of the compounds, are summarized in Tables A-1 and A-2.

2. Methyl N-Fluorocarbamate

A solution of 75 g (1.0 mole) of methyl carbamate in 500 ml of water was fluorinated at 0 to 5°C, with fluorine diluted with nitrogen (1:4), until 22.5 liters of fluorine was consumed (3.0 hours). The reaction mixture was extracted with ten 50-ml portions of diethyl ether. The combined ethereal extracts were dried and filtered, and the filtrate was concentrated. The residual liquid was fractionated at reduced pressure to give 22 g of methyl N-fluorocarbamate. Approximately 30 g of starting material was recovered from the distillation residue.

3. Ethyl N-Fluorocarbamate

A solution of 270 g (3.0 moles) of ethyl carbamate in 3000 ml of water was fluorinated as described above until 80 liters of fluorine was consumed (7.0 hours). The reaction mixture was worked up in an analogous manner

Page A-7

CONFIDENTIAL

CONFIDENTIAL

Report No. 2945

as described above to give 75 g of ethyl N-fluorocarbamate. The distillation residue amounted to 150 g and contained mainly starting material and some more of N-fluorocarbamate, but further fractionation became difficult due to the proximity of the boiling points of the two components.

In the two experiments described above, as well as in the fluorination of isopropyl and n-butyl carbamate, in a few instances, two -80°C traps were placed in the gas exit line; these traps produced a partial condensation of gaseous reaction products. The liquid condensates were analyzed by infrared, using a gas cell; in all cases, the condensates consisted of a mixture of difluoramine and carbon dioxide.

4. Alkyl N,N-Difluorocarbamates

Elemental analyses, physical properties, and NMR spectra of N,N-difluorocarbamates are summarized in Tables A-3 and A-4.

5. n-Butyl N,N-Difluorocarbamate

A solution of 43 g (0.8 mole) of n-butyl carbamate in 400 ml of acetonitrile was fluorinated at 0 to 5°C until approximately 45 liters of fluorine was consumed; fluorination time was 1.5 hours. The fluorination mixture was distilled at 25 to $30^{\circ}\text{C}/20$ to 25 mm and n-butyl N,N-difluorocarbamate was removed together with the solvent. The residual liquid was worked up to give 13 g of n-butyl N-fluorocarbamate, and 20 g of the starting material.

The distillate was added to 750 ml of ice water, resulting in the separation of two phases. The organic phase was washed with two 200-ml portions of ice water and dissolved in 200 ml of methylene chloride. The methylene chloride solution was dried, filtered, concentrated and the residual liquid distilled to give 53 g of n-butyl N,N-difluorocarbamate, b.p. $65^{\circ}\text{C}/60$ mm, n_{D}^{25} 1.3665 (43% yield).

6. Ethyl N,N-Difluorocarbamate

A solution of 22.5 g (0.25 mole) of ethyl carbamate in 150 ml of n-butyronitrile was fluorinated at 0 to -5°C until 12 liters of fluorine gas was

Page A-8

CONFIDENTIAL

CONFIDENTIAL

Report No. 2945

consumed; to the fluorination mixture was added 30 g of sodium fluoride. To remove the dissolved hydrogen fluoride present in the solution, the resulting mixture was stirred vigorously at 25°C for a few hours. The filtered solution was fractionated and N,N-difluorocarbamate, b.p. 31 to 35°C/100 mm, was removed from the solution. The crude material, containing several impurities (mainly *n*-butyronitrile) could not be purified further by fractionation and an analytical sample was obtained by gas chromatography.

7. Isopropyl N,N-Difluorocarbamate

A solution of 103 g (1.0 mole) of isopropyl carbamate in 500 ml of acetonitrile was fluorinated at +5 to -5°C until 1 mole of fluorine was consumed. The fluorination mixture was concentrated at 30°C/20 to 25 mm and a mixture of solvent and N,N-difluorocarbamate was removed. The residual liquid, amounting to 82 g, was dissolved in 100 ml of methylene chloride and the solution was dried and deacidified by addition of 20 g of sodium fluoride and 20 g of anhydrous sodium sulfate. The filtered solution was concentrated and the residual liquid fractionated to give 44 g of isopropyl N-fluorocarbamate (41% yield). From the distillation residue 35 g of starting material was recovered.

The acetonitrile-NF₂CO₂C₃H₇ fraction was added to 1200 ml of ice-water, resulting in the separation of two phases. The organic phase was washed with two 150 ml portions of cold water and then dissolved in 50 ml of methyl formate. The methyl formate solution was dried, filtered, and concentrated. The residual liquid was fractionated to give 18 g of isopropyl N,N-difluorocarbamate (13% yield), b.p. 41 to 42°C/60 mm.

In an analogous experiment using a 2:1 mole ratio of fluorine to isopropyl carbamate, the yield of isopropyl N,N-difluorocarbamate increased to 65%.

8. Sodium Salt of Ethyl N-Fluorocarbamate

Ethyl N-fluorocarbamate, 3.21 g (0.03 mole) was added dropwise with stirring at 0 to 3°C to a solution of 1.2 g (0.03 mole) of sodium hydroxide in 20 ml water. A pale-yellow solution resulted, from which N-fluorocarbamate

Page A-9

CONFIDENTIAL

CONFIDENTIAL

Report No. 2945

could not be extracted with diethyl ether or methylene chloride. After standing for 10 min at 0°C, the alkaline solution was acidified with 20% sulfuric acid. The acidic solution was extracted with seven 15 ml portions of diethyl ether. The combined extracts were worked up resulting in the recovery of 2.3 g of ethyl N-fluorocarbamate.

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

Ethyl N-fluorocarbamate, 2.7 g (0.025 mole), was added at 0 to 5°C with stirring to a suspension of 1.0 g (0.025 mole) of sodium hydroxide in 15 ml of absolute ethanol. An evacuated infrared gas cell was connected in series with the reactor. At the end of the addition of the carbamate (which took 5 min), the reaction mixture was allowed to warm to 20 to 25°C. Sodium hydroxide gradually dissolved and the reaction mixture warmed by itself to 35 to 40°C. At this point, external cooling was applied and the reaction mixture was kept at 35 to 38°C until all sodium hydroxide dissolved and the exothermic reaction ceased. The gaseous reaction products evolved during the warming period and were trapped in the infrared gas cell. The gas contained mainly carbon dioxide, contaminated with some ethylene.

At the end of the reaction the ethanolic solution was concentrated to 5 to 8 ml and the residual material added to 100 ml of ice-water. The aqueous solution was extracted with four 20-ml portions of methylene chloride and the combined extracts were worked up by fractionation to give: 0.8 g of a liquid, b.p. 50 to 55°C/0.1 to 0.3 mm, n_D^{25} 1.4228; and 0.8 g of a liquid, b.p. 85 to 95°C/0.1 mm, n_D^{25} 1.4375. The material of the second fraction solidified while standing; this crude solid was purified by crystallization from n-pentane to give 0.6 g of a white microcrystalline solid, m.p. 46 to 47°C. The purified material was identified as iminodicarboxylic acid diethyl ester, $\text{NH}(\text{CO}_2\text{C}_2\text{H}_5)_2$; it has a reported m.p. of 47°C (Reference 4).

Anal. Calc'd for $\text{C}_6\text{H}_{11}\text{NO}_9$: C, 44.71; H, 6.86; N, 8.67.

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

CONFIDENTIAL

Report No. 2945

10. Decomposition of Ethyl N-Fluorocarbamate with Methanolic Sodium Methoxide

Methanolic sodium methoxide was prepared by dissolving 1.15 g of metallic sodium in 25 ml of dry methanol. To this solution was added (drop-wise with stirring over a period of 10 min at 0 to 3°C), 5.4 g (0.05 mole) of ethyl N-fluorocarbamate. The reaction was exothermic, but the temperature was controlled by an ice-water bath. At the end of the addition, the cooling bath was removed and in a matter of minutes the reaction mixture heated to the boiling point of methanol.

The reaction was repeated with the same quantities of starting materials, except that methanolic sodium methoxide solution was diluted with 25 ml of anhydrous diethyl ether before addition of the N-fluorocarbamate. At the end of the run, the reaction mixture was allowed to warm up to 20 to 25°C, and was allowed to stand for 45 min. The solution was concentrated at room temperature at reduced pressure to remove the solvents. The residual viscous oil was treated with 50 ml of methylene chloride resulting in deposition of a white solid, which was removed by filtration and identified (infrared spectrum) as sodium fluoride, wt 2.0 g. The methylene chloride filtrate was concentrated and the residual liquid was subjected to fractionation. After removal of ca. 1.0 ml of an unidentified liquid, b.p. 25 to 29°C/0.1 to 0.3 mm, a semi-solid residue remained and was purified by crystallization from n-pentane to give 0.7 g of a white microcrystalline solid, m.p. 64°C, which was identified as methyl ethyl ester of iminodicarboxylic acid, $\text{CH}_3\text{OOCNHCO}_2\text{C}_2\text{H}_5$.

Anal. Calc'd for $\text{C}_5\text{H}_9\text{NO}_4$: C, 40.82; H, 6.17; N, 9.5.

Found: C, 41.1; H, 6.1; N, 9.7.

11. Ethyl N-Chloro-N-fluorocarbamate

The reaction was carried in a 100-ml four-necked round-bottomed flask equipped with a stirrer, thermometer, and gas inlet and outlet tubes. The sodium salt of ethyl N-fluorocarbamate was prepared by dissolving 4.3 g (0.04 mole) of ethyl N-fluorocarbamate at 0 to 5°C in a solution of 1.6 g (0.04 mole) of sodium hydroxide in 25 ml of water. The solution, together with 25 ml of methylene chloride was placed into the reaction flask and gaseous chlorine (0.04 mole) was

Page A-11

CONFIDENTIAL

CONFIDENTIAL

Report No. 2945

passed into the vigorously stirred solution at 0 to 5°C over a period of 30 to 45 min. At the end of the run, the phases were separated and the aqueous phase extracted with two 25-ml portions of methylene chloride. The organic phase and methylene chloride extracts were combined, dried, filtered and worked up to give 3.2 g of a colorless liquid, b.p. 45°C/60 to 65 mm, n_D^{25} 1.4015, which was identified as ethyl N-chloro-N-fluorocarbamate.

Anal. Calc'd for $C_3H_5ClFNO_2$: C, 25.46; H, 3.56; N, 9.90; F, 13.42.

Found: C, 25.8; H, 3.5; N, 9.8; F, 13.0.

The infrared spectrum of the material showed C=O absorption peak at 5.55 to 5.6 microns; NH absorption was absent.

The distillation residue, after removal of N-chloro-N-fluorocarbamate, on further fractionation gave 1.1 g of a colorless liquid, b.p. 55°C/0.1 mm, n_D^{25} 1.4145, which was identified diethyl N-fluoroiminodicarboxylate by comparing its infrared spectrum and its physical properties with those of an authentic sample (see below).

12. Ethyl N-Bromo-N-fluorocarbamate

Ethyl N-bromo-N-fluorocarbamate was synthesized in 75% yield by reacting aqueous sodium salt of ethyl N-fluorocarbamate with stoichiometric amount of bromine in the same manner as described above for the N-chloro derivative. The crude material, b.p. 30°C/0.1 to 0.2 mm, n_D^{25} 1.4425, was redistilled and a middle cut, b.p. 30°C/0.1 mm, n_D^{25} 1.4421, was taken for analysis.

Anal. Calc'd for $C_3H_5BrFNO_2$: C, 19.36; H, 2.7; N, 7.53; Br, 42.96; F, 10.20.

Found: C, 19.8; H, 2.4; N, 7.6; Br, 45.0; F, 10.6.

The infrared spectrum of ethyl N-bromo-N-fluorocarbamate was practically identical with that of ethyl N-chloro-N-fluorocarbamate.

Diethyl fluoriminodicarboxylate, 1.5 g, was obtained on fractionation of the distillation residue.

Page A-12

CONFIDENTIAL

CONFIDENTIAL

Report No. 2945

13. Diethyl Fluoriminodicarboxylate

The sodium salt of ethyl N-fluorocarbamate was prepared by dissolving, at 0 to 5°C, 5.4 g (0.05 mole) of ethyl N-fluorocarbamate in a solution of 2.0 g (0.05 mole) of sodium hydroxide in 50 ml of water. The solution was placed in a 100-ml three-necked round-bottomed flask equipped with a dropping funnel, thermometer, and a stirrer. To the vigorously stirred solution was added from the dropping funnel at 5 to 10°C, 5.4 g (0.05 mole) of ethyl chloroformate over a period of 10 min. The reaction was mildly exothermic and a pale-yellow oil separated as the reaction progressed. The reaction mixture was stirred for an additional 10 min and then extracted with two 25 ml portions of methylene chloride. The combined extracts were dried, filtered, the filtrate concentrated, and the residual liquid distilled to give 6.5 g of the produce, b.p. 55°C/0.1 to 0.3 mm, n_D^{25} 1.4145. Distillation residue amounted to 1.0 g.

Anal. Calc'd for $C_6H_{10}FNO_4$: C, 40.22; H, 5.63; N, 7.82; F, 10.61.

Found: C, 40.3; H, 5.8; N, 7.7; F, 10.9.

14. Ethyl N-Fluoro-N-methylcarbamate

Aqueous sodium salt of ethyl N-fluorocarbamate was prepared as above from 8.6 g (0.08 mole) of ethyl N-fluorocarbamate. To the solution was added, with stirring, 5.05 g (0.04 mole) of dimethylsulfate and the reaction mixture was stirred vigorously at 5 to 10°C; external cooling was required for a period of 60 to 70 min. A white solid (sodium sulfate) and a pale-yellow oil gradually separated. The reaction mixture was extracted with three 25-ml portions of methylene chloride, and the combined extracts worked up to give 4.5 g of ethyl N-fluoro-N-methylcarbamate, b.p. 50°C/25 mm, n_D^{25} 1.3870. The infrared spectrum showed strong carbonyl and the absence of NH absorption at 2.8 to 3.4 microns.

Anal. Calc'd for $C_4H_8FNO_2$: C, 39.67; H, 6.66; N, 11.57; F, 15.69.

Found: C, 39.3; H, 6.6; N, 11.97; F, 15.2.

Page A-13

CONFIDENTIAL

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Report No. 2945

15. Dichlorofluoramine

a. From Ethyl N-Fluorocarbamate

Sodium hypochlorite, 150 ml of 5.4% aqueous solution, was placed into a 250-ml four-necked round-bottomed flask equipped with a stirrer, a dropping funnel, a thermometer, and gas-outlet tube connected in series with a -80°C trap. The solution was cooled to 0 to 5°C , and to it was added, dropwise with stirring and cooling, 5.4 g (0.05 mole) of ethyl N-fluorocarbamate, over a period of 20 to 25 min. During this time, some water-insoluble heavy liquid accumulated in the reactor. The reaction mixture was allowed to warm to 25 to 28°C , during which time the product evaporated and recondensed in the -80°C trap. The material, purified by trap-to-trap distillation, amounted to 1.8 ml at -20°C . The infrared spectrum of the material was identical with that reported (Reference 5) for dichlorofluoramine.

b. From Ethyl N-Chloro-N-fluorocarbamate

Using a similar apparatus as above, 0.7 g of ethyl N-chloro-N-fluorocarbamate was reacted at 0 to 5°C with 20 ml of 5.4% aqueous sodium hypochlorite, resulting in the preparation of 0.3 ml (at -20°C) of dichlorofluoramine.

16. Difluoramine

Thirty ml of 25% aqueous sulfuric acid was placed in a 50-ml three-necked, round-bottomed reaction flask equipped with a magnetic stirrer, a dropping funnel, a thermometer, and a gas-outlet tube connected in series with a -80°C cold trap. Isopropyl N,N-difluorocarbamate, 4.2 g (0.03 mole), was placed in the dropping funnel. The whole apparatus was flushed with nitrogen. The gas-outlet tube was protected from air throughout the run by a slow nitrogen gas stream. The carbamate was added dropwise with stirring to the reactor containing sulfuric acid, but little or no reaction was noticed at room temperature. The reaction mixture was gradually warmed to 65 to 70°C , at which temperature difluoramine was liberated rapidly; hydrolysis was completed in 30 min. During this time, 1.05 ml of liquid difluoramine accumulated in the -80°C trap. At the

Page A-14

CONFIDENTIAL

CONFIDENTIAL

Report No. 2945

end of the run, the generator was cooled to 25°C and the whole system was flushed with nitrogen gas. A sample of the material of the -80°C trap was allowed to evaporate in an evacuated infrared gas cell by lowering the dry ice-acetone cooling bath. The infrared spectrum of the product was identical with that reported for difluoramine (Reference 6), but the material was contaminated with 5 to 15% carbon dioxide.

17. Chlorodifluoramine

Using a similar apparatus as above, 0.3 g of *n*-butyl N,N-difluorocarbamate was added to 0 to 5°C to 20 ml of 5.3% aqueous sodium hypochloride. The cooling trap was omitted; instead the gas exit line was connected in series with an evacuated infrared gas cell. No gaseous products were liberated, indicating that the reaction was either too slow at 0 to 5°C, or more likely, that chlorodifluoramine was soluble in aqueous hypochloride. After 15 min the reaction mixture was warmed to 30 to 35°C and a sample of the gas was collected in the gas cell. The infrared spectrum of the gas was identical with that reported for chlorodifluoramine (Reference 7).

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Page A-15

CONFIDENTIAL

CONFIDENTIAL

Report No. 2945

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Page A-16

CONFIDENTIAL

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Report No. 2945

TABLE A-1

ALKYL N-FLUOROCARBAMATES, NHFCO₂R

R	Yield %	Boiling Point °C/mm	n _D ²⁵	Elemental Analysis, %							
				Calculated				Found			
				C	H	N	F	C	H	N	F
CH ₃	27	62-3/26	1.3895	25.81	4.33	15.05	20.42	25.5	4.4	15.0	20.4
C ₂ H ₅	24	30/0.1-0.3	1.3950	33.64	5.65	13.08	17.74	33.4	5.5	13.0	17.8
i-C ₃ H ₇	41	29-30/0.1	1.3970	39.67	6.66	11.57	15.69	39.5	6.4	11.5	15.4
n-C ₄ H ₉	20	36-7/0.1	-	44.44	7.46	10.37	14.06	44.8	7.4	10.1	14.0

Table A-1

CONFIDENTIAL

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Report No. 2945

TABLE A-2

FLUORINE AND PROTON NMR SPECTRA
OF ALKYL N-FLUOROCARBAMATES, NHFCO₂R

R	56.4-mc F ¹⁹ NMR Spectra ^a		60-mc H ¹ NMR Spectra ^b		R, ppm
	NHFCO ₂ R Doublet Position ppm	Doublet Splitting cps	NHFCO ₂ R Doublet Position ppm	Doublet Splitting cps	
CH ₃ ^c	+119.1	56.0	10.10	58.0	-CO ₂ CH ₃ singlet at 4.02
C ₂ H ₅ ^d	+116.00	55.7	9.78	55.7	-CO ₂ CH ₂ CH ₃ triplet at 1.33 -CO ₂ CH ₂ CH ₃ quartet at 4.32
i-C ₃ H ₇ ^d	+115.70	55.5	9.60	55.9	-CH(CH ₃) ₂ doublet at 1.33 -CH(CH ₃) ₂ septet at 5.07
n-C ₄ H ₉ ^d	+114.88	56.1	9.42	55.5	-OCH ₂ - triplet at 4.26 -OCH ₂ CH ₂ CH ₂ CH ₃ multiplet with max. intensity of 9 cps -O(CH ₂) ₃ CH ₃ at 0.94

- a. CFCl₃ used as internal standard.
- b. TMS used as internal standard.
- c. In CHCl₃ solution.
- d. CDCl₃ used as solvent.

Table A-2

CONFIDENTIAL

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Report No. 2945

TABLE A-3

ALKYL N,N-DIFLUOROCARBAMATES, $\text{NF}_2\text{CO}_2\text{R}$

R	Yield %	Boiling Point °C/mm	Elemental Analysis, %							
			Calculated				Found			
			C	H	N	F	C	H	N	F
CH_3	30	37-8/150 ^a	21.63	2.72	12.61	34.21	22.0	2.9	12.2	
C_2H_5	40	31-5/100 ^a	28.81	4.03	11.20	30.38	29.2	4.4	11.0	
$\text{i-C}_3\text{H}_7$	65	41-2/60	34.54	5.08	10.07	27.32	34.8	4.7	9.9	26.5
$\text{n-C}_4\text{H}_9$ ^b	43	65/60	39.21	5.92	9.15	24.82	39.2	6.2	9.1	25.1

a. Crude material. Final purification by gas chromatography.

b. n_D^{25} 1.3665.

Table A-3

CONFIDENTIAL

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Report No. 2945

TABLE A-4

FLUORINE AND PROTON NMR SPECTRA^a
OF ALKYL N,N-DIFLUOROCARBAMATES, $\text{NF}_2\text{CO}_2\text{R}$

R	56.4-mc F^{19} Spectra ^b $\text{NF}_2\text{CO}_2\text{R}$ Singlet ppm	60-mc H^1 Spectra ^c ; R, ppm
CH_3	-	$-\text{CO}_2\text{CH}_3$, singlet at 4.10
C_2H_5	-	
$\text{i-C}_3\text{H}_7$	-32.74	$-\text{CH}(\text{CH}_3)_2$ septet at 5.19 $-\text{CH}(\text{CH}_3)_2$ doublet at 1.44
$\text{n-C}_4\text{H}_9$	-32.8	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ irregular triplet at 0.98 $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ complex multiplet with maximum intensity at 96 cps $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ triplet at 4.42

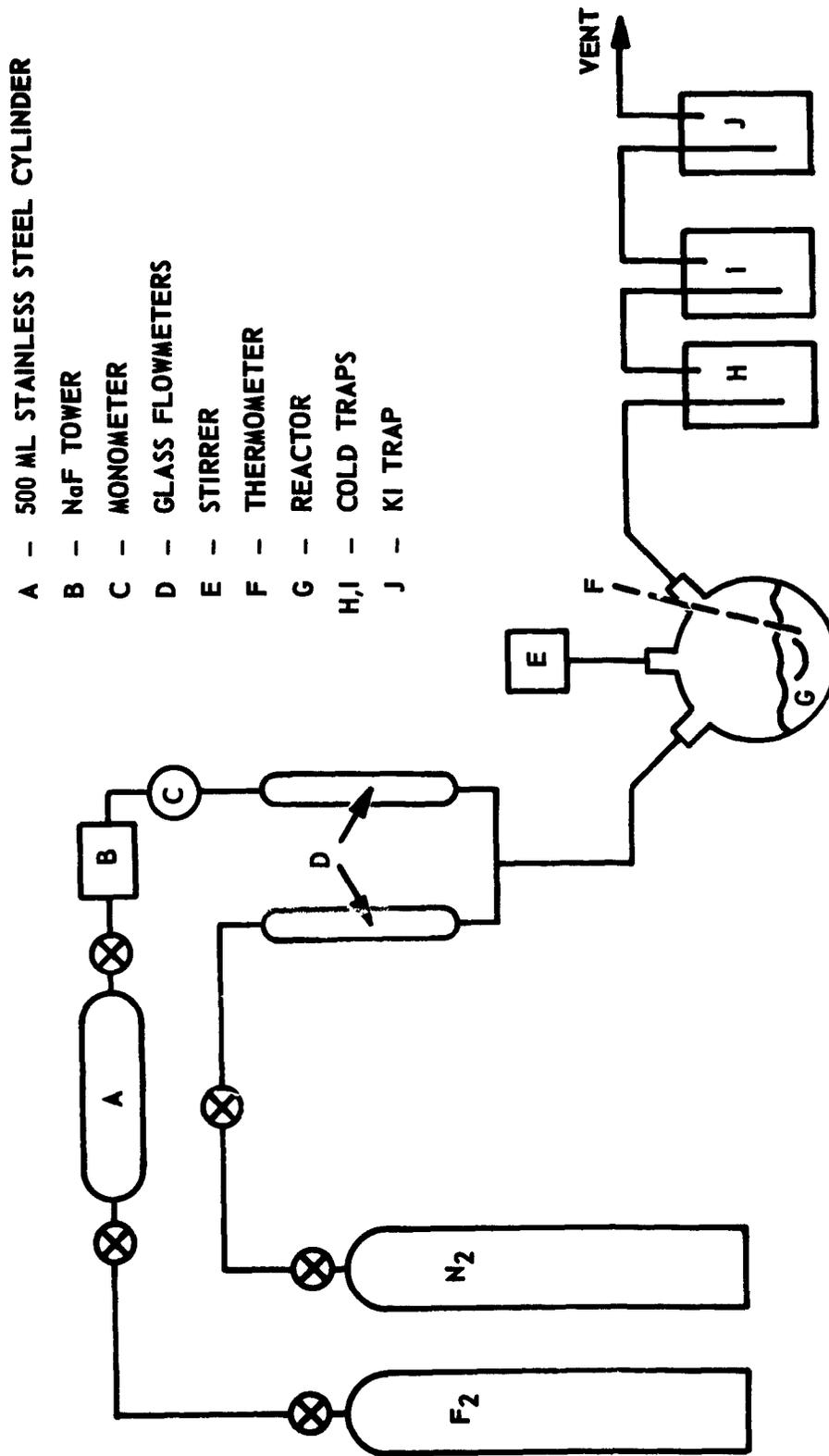
a. In CDCl_3 solution.

b. CFCl_3 used as internal reference.

c. TMS used as internal reference.

Table A-4

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Direct Fluorination Apparatus

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