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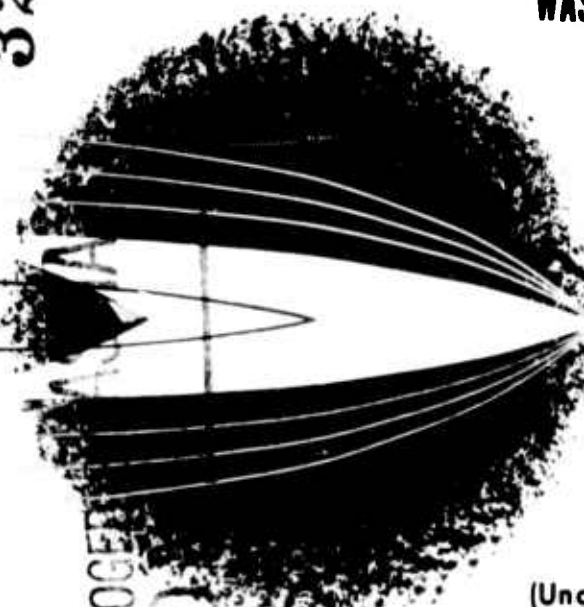
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RESEARCH IN FLURO-NITRO COMPOUNDS

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



Chemical Division

XEROX

Aerojet-General CORPORATION

AZUSA, CALIFORNIA

THE
GENERAL
TIRE

SACRAMENTO, CALIFORNIA

A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

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December 1961

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AEROJET-GENERAL CORPORATION
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Report No. 0235-01-12

ABSTRACT

The reaction of methallylacetone with difluoramine in sulfuric acid gave 2,5,5-trimethyl-2(difluoramino)tetrahydrofuran. Methyl acrylate gave methyl β -difluoramino propionate. 3-Methyl-2-pentanone, n-heptaldehyde and 2,7-octanedione gave the expected gem-difluoramines. The reactions of ethoxyacetylene, cyclobutanone and dicyclohexylcarbodiimide were carried out, but the products have not yet been fully characterized.

Fluorination of aqueous methylene- and ethylenedicarbamates gave a mixture of products. Ethyl difluoraminoethylcarbamate and ethyl- β -difluoraminoethylfluorocarbamate respectively, were the main reaction products. N,N'-Difluoro derivatives were also obtained in both cases. Fluorination of aqueous methylenediacetamide and methylenediformamide yielded only trace amounts of bis-(difluoramino)methane. Fluorination of allyl- and arylureas and cyanoguanidine gave N,N'-difluorourea as the main reaction product.

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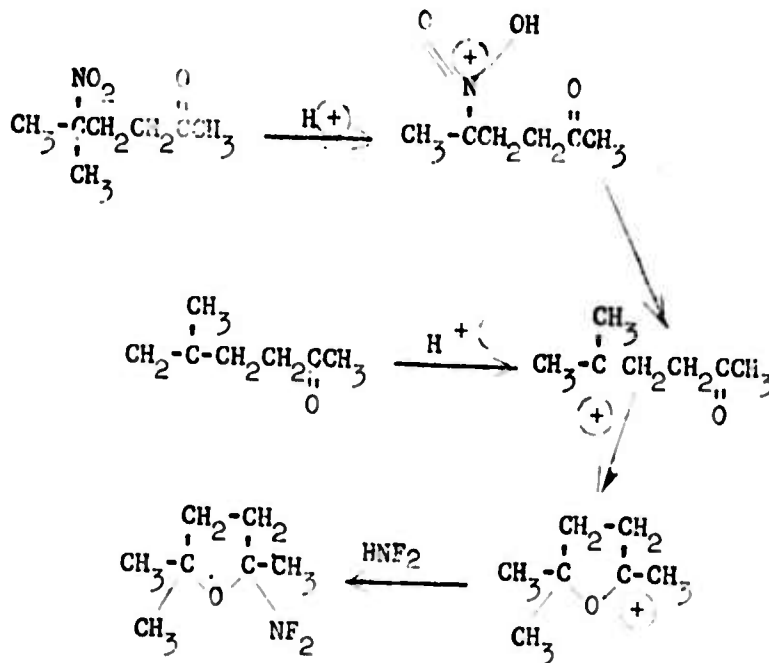
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Another example of a 5-ketoolefin, methallyl acetone, has also been investigated. The purpose of this experiment was both to show the generality of this reaction and to provide additional structure proof for the product formed from 5-methyl-5-nitro-2-hexanone under these conditions, by a novel denitration reaction.* The products of these two reactions were found to be identical by comparing their physical properties and infrared spectra.



Another 5-ketoolefin which was examined in this reaction was 2-methyl-2-heptene-6-one, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$. In this case the formation of a tetrahydrofuran derivative would require anti-Markownikoff protonation of the double bond, so it is not surprising that this reaction was not observed. A carbonyl-containing NF_2 compound was formed, which was tentatively identified as 2-methyl-2-(difluoramino)-6-heptanone. The carbonyl group was probably not replaced because of an insufficient reaction time.



* Aerojet-General Report 0235-01-11, 14 July 1961, p 3 (Confidential)

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b. Conjugated Olefins

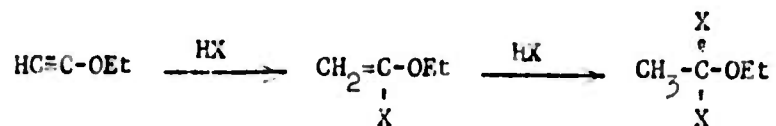
The 1,4- addition of difluoramine to methyl vinyl ketones and acrylic acid has been reported.* Several other examples of this reaction have been investigated. Thus the reaction of methyl acrylate with difluoramine in sulfuric acid proceeded similarly, with the formation of methyl β -(difluoramino)propionate in high yield. The infrared spectrum of this product is shown in Figure 1.



Methyl methacrylate and methyl methacrylate, however, did not react under these conditions and the starting materials were recovered. Styrene, acrylamide, and 2-methyl-1-butene-3-yne underwent decomposition or polymerization and no NF_2 compounds were isolated. These reactants, with the exception of acrylamide (which was dissolved in the sulfuric acid prior to the reaction), were added to a refluxing mixture of difluoramine and sulfuric acid. Decomposition might be prevented by adding the acid last.

c. Acetylenes

Ethoxyacetylene reacts with hydrogen halides to form the unsaturated halides and gem-dihalides.*



The addition of difluoramine to ethoxyacetylene would be expected to give initially 1-ethoxy-1-(difluoramino) ethylene(I). However, several subsequent reaction paths are possible. A fluorine atom could migrate from nitrogen to carbon to form 1-fluorimino-1-ethoxy-2-fluoroethane(II). The addition of a second mole of difluoramine to I might take place faster than the rearrangement to give

* Aerojet-General Report 0235-01-11, 14 July 1961 (Confidential)

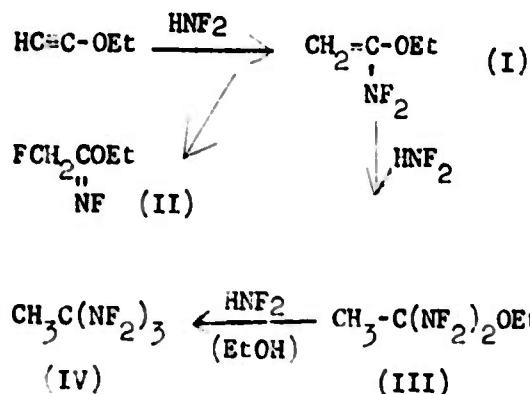
** K. Broekema, S. Vander Werf and J. F. Arens, Rec. Trav. Chim. 77 (1958)

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1,1-bis(difluoramino)-1-ethoxyethane (III), and this compound might react farther to give 1,1,1-tris(difluoramino)ethane (IV).



The reaction of difluoramine with ethoxyacetylene was carried out in the absence of solvents or catalysts, simply by allowing difluoramine to reflux over the ethoxyacetylene at atmospheric pressure. A complex mixture of products was formed, of which the two major components were isolated by gas chromatography. The infrared spectra (Figures 2 and 3) indicate NF absorption as well as peaks due to olefin or fluorimine (6.1 to 6.2 μ) and, in the case of the compound with the smallest retention time, possibly carbonyl (5.65, 5.75 μ). Analytical results are not yet available. Further work with this reaction will include the investigation of acid catalysts.

The formation of gem-difluoramines by the addition of difluoramine in sulfuric acid to simple acetylenes apparently involves the hydration of the triple bond.* An attempt was made to carry out the addition of difluoramine to 3-hexyne in the presence of mercuric oxide to test for a possible catalysis of the direct addition of difluoramine. In this experiment, the gem-difluoramine was isolated, as well as some 3-hexanone. The reaction of difluoramine with 3-hexyne in fuming sulfuric acid was also attempted, but only a trace of oxidizing product was isolated.

* Aerojet-General Report 0235-01-11, 14 July 1961, p. 6 (Confidential).

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II Technical Discussion, A (cont.)

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d. Simple Ketones and Aldehydes

The reaction of cyclobutanone with difluoramine in sulfuric acid previously resulted in a fume-off*. Another attempt has now been made to carry out this reaction. The addition of cyclobutanone to difluoramine and sulfuric acid liberated a large amount of heat, but by very slow addition of the ketone, the reaction could be controlled. No material insoluble in the acid was formed, but quenching the acid with ice gave a material with infrared absorption in the carbonyl and NF regions. The elemental analysis was in fair agreement with theoretical 3-fluorimino-2-butanone, $\text{CH}_3\overset{\text{NF}}{\text{C}}\text{COCH}_3$. The identification of this material is still in progress.

3-Methyl-2-pentanone was converted to the corresponding gem-difluoramine to determine whether α -methyl groups interfere with the reaction. The reaction proceeded normally.

n-Heptaldehyde was treated with difluoramine in fuming sulfuric acid to prepare 1,1-bis(difluoramino)heptane. This product was prepared as a stable model compound for studying the dehydrofluorination of terminal gem-difluoramines to prepare the trifluoroamidines. However, because of reports that this reaction had been carried out elsewhere, we discontinued this work.

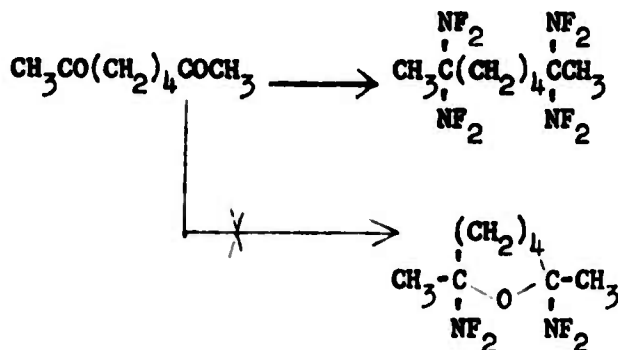
The reaction of 2,7-octanedione with difluoramine was also studied. It was of interest to see whether this reaction would give a heterocyclic difluoramino compound, as was found for acetonylacetone, or the gem-difluoramine.** Workup of the reaction mixture gave a material with some carbonyl absorption in the infrared. This peak was removed by washing the product with concentrated sulfuric acid. The infrared spectrum (Figure 4) and preliminary analytical data showed that the product was 2,2,7,7-tetrakis(difluoramino) octane. The lack of ether absorption before and after the purification indicate that the cyclic product was not formed.

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

** Ibid.

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e. Miscellaneous

The reaction of 1,3,3-triethoxybutane with difluoramine in sulfuric acid gave an NF compound which has not yet been identified. Although the elemental analysis is in approximate agreement with theoretical for 1-ethoxy-3,3-bis(difluoramino) butane, the infrared spectrum shows extremely strong carbonyl absorption. Further work will be done with this material.

The addition of difluoramine to dicyclohexylcarbodiimide was studied as a possible means of preparing a material with four nitrogen atoms connected to a carbon. In the initial experiment, difluoramine was refluxed over the carbodiimide at atmospheric pressure for 4 hrs without an added catalyst or solvent. The infrared spectrum of the product indicated mainly starting material, but with major new peaks at 6.0 and 11.7 μ . These would suggest the formation of the monoadduct, $\text{C}_6\text{H}_{11}\text{N}=\text{C}(\text{NF}_2)\text{NHC}_6\text{H}_{11}$. This reaction was then repeated, with the addition of sulfuric acid to the refluxing solution of the diimide in difluoramine. In this case a large yield of a white oxidizing solid, m.p. 48 $^\circ$, was isolated. This material has not yet been identified.

2. Experimental

a. 2,5,5-Trimethyl-2-(difluoramino)tetrahydrofuran

To a refluxing mixture of 6 g difluoramine and 15 ml conc sulfuric acid was added, dropwise, 2.28 g (0.02 mole) of methallylacetone. The solution became slightly yellow during the addition. After 3-1/2 hr the excess

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difluoramine was removed and the solution was poured over 150 ml of ice. The product was extracted with three 50-ml portions of methylene chloride, washed with 50 ml of water and dried over sodium sulfate. The solution was filtered and the solvent distilled off. The remaining liquid was distilled to give 0.66 g 2,5,5-trimethyl-2-(difluoramino)tetrahydrofuran, identical to the product prepared from 5-methyl-5-nitro-2-hexanone.*

b. Reaction of 2-Methyl-2-heptene-6-one with Difluoramine

Difluoramine (8 g) was refluxed into 20 ml of concentrated sulfuric acid. 2-Methyl-2-heptene-6-one (2.52 g, 0.02 mole) was added dropwise. After 4 hrs, the excess difluoramine was removed and the solution was poured over 150 ml of ice and the product extracted with 150 ml of methylene chloride. The methylene chloride solution was washed with 50 ml of water, dried over sodium sulfate, and the solvent distilled off. Distillation of the residue gave 0.4 g 2-methyl-3-(difluoramino)-6-heptanone.

Anal. calc'd for $C_8H_{13}ONF_2$: C, 53.5; H, 8.4; N, 7.8

Found: C, 50.0; H, 7.48; N, 7.60

c. Methyl β -Difluoraminopropionate

Methyl acrylate (2.92 g, 0.034 mole) was added to a refluxing mixture of 8 g of difluoramine and 17 ml of concentrated sulfuric acid. A pale yellow, homogeneous solution formed. The excess difluoramine was removed after 3-1/2 hr and the solution was poured over 150 ml of crushed ice. A heavy layer separated and was extracted with four 50-ml portions of methylene chloride. The solution was washed with 50 ml of water and dried over sodium sulfate. The solvent was removed by distillation. Distillation of the residue gave 3.5 g (0.025 mole, 73.5% yield) of methyl β -difluoraminopropionate, b.p. 47°C/20 mm, n_D^{25} 1.3795.

*Aerojet-General Report 0235-01-11, 14 July 1961 as corrected in Errata, 7 August 1961, Figure 4.

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Anal. Calc'd for $C_4H_7O_2NF_2$: C, 34.53; H, 5.04; N, 10.07

Found: C, 34.25; H, 5.22; N, 10.2

d. Reaction of Difluoramine with Ethoxyacetylene

Difluoramine (5 g) was allowed to reflux over 1.4 g (0.02 mole) of ethoxyacetylene for 4-1/2 hr. The excess difluoramine was removed, and the product was vacuum-transferred at 0.1 mm to a -80° trap. Fractions of the two major components were trapped by gas chromatography and the infrared spectra were obtained. Elemental analyses have not yet been obtained.

e. 3-Methyl-2,2-bis(difluoramino) pentane

Difluoramine (8 g) was refluxed over 15 ml conc sulfuric acid, and 2.5 g (0.025 mole) 3-methyl-2-pentanone was added dropwise. During the 3-hr reflux period a colorless layer separated from the solution. The excess difluoramine was removed, and the product was vacuum-transferred into a -80° C trap at 1 mm to yield 1.39 g of colorless liquid. Distillation gave 0.43 g 3-methyl-2,2-gem(difluoramino)pentane, b.p. 59° C/27 mm.

Anal. calc'd for $C_6H_{12}N_2F_4$: C, 38.2; H, 6.4; N, 14.9; F, 40.4

Found: C, 38.0; H, 7.0; N, 14.1; F, 38.4

f. 2,2,7,7-tetrakis(Difluoramino)octane

A solution of 2.13 g (0.015 mole) of 2,7-octanedione in 17 ml of conc sulfuric acid was prepared at 0° C. Difluoramine (7 g) was generated and allowed to reflux over this solution for 4-1/2 hr. The excess difluoramine was then swept out and the acid was poured over 150 ml of crushed ice. The product was extracted with three 50-ml portions of methylene chloride. The methylene chloride solution was then washed with 50 ml of water, dried over sodium sulfate and concentrated by distillation. Vacuum distillation of the residue gave 1.3 g of colorless liquid, b.p. 71 to 72° /0.1 mm, which showed carbonyl absorption in the infrared spectrum. This material was stirred with 4 ml of conc sulfuric acid and extracted with 6 ml of methylene chloride. The

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II Technical Discussion, A (cont.)

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solution was washed with two 5-ml portions of water and dried over sodium sulfate, and the solvent was removed. The residue was 0.53 g of white solid, m.p. 60°.

Anal. calc'd for $C_8H_{14}N_4F_8$: C, 30.2; H, 4.40; N, 17.6; F, 47.5

Found: C, 29.3; H, 3.99; N, 16.5; F, 44.8

When the acid layer from the purification was poured over ice, no precipitate was formed.

g. Reaction of Cyclobutanone with Difluoramine

To a refluxing mixture of 30 ml of sulfuric acid and 6g of difluoramine, 1.4 g (0.02 mole) of cyclobutanone was added dropwise. A high reaction exotherm required very slow addition of the cyclobutanone. After 4 hr, the homogeneous solution was poured over 150 ml of ice. The product was extracted with three 50-ml portions of methylene chloride. The combined methylene chloride solution was then washed with 50 ml of water and dried over sodium sulfate, and the solvent was distilled off through a 6-in. packed column. Distillation of the residue gave 0.4 g of a colorless liquid, b.p. 41°/0.1 mm.

Anal. found: C, 44.2; H, 5.42; N, 12.6, F, 17.6.

h. Reaction of 1,3,3-Triethoxybutane with Difluoramine

1,3,3-Triethoxybutane (20 g, 0.0105 mole) was added dropwise to a refluxing mixture of 7 g of difluoramine and 18 ml of conc sulfuric acid. After 4 hrs the mixture was poured over 150 ml of crushed ice. The product was extracted with three 50-ml portions of methylene chloride and the organic solution was washed with 50 ml of water and dried over sodium sulfate. The methylene chloride was distilled through a 6 in. packed column and the residue was distilled to yield 0.8 g of colorless liquid, b.p. 37°/4mm. The infrared spectrum showed a strong peak at 5.8 μ , as well as peaks at 7.0, 7.3, 8.6, 10.2, 11.0 and 12.2 μ .

Anal. found: C, 30.4; H, 4.65; N, 14.5; F, 40.6.

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3. AQUEOUS FLUORINATION (V. Grakauskas)

1. Discussion

a. Fluorination of Dicarbamates

It has been shown that simple carbamates undergo direct fluorination to give the corresponding NF derivatives.* This work has been extended to geminal and vicinal dicarbamates with the objective of synthesizing the corresponding bis(difluoramino) derivatives.

An aqueous suspension of diethyl methylenedicarbamate was fluorinated until three moles of fluorine per mole of the dicarbamate were consumed. A trace of bis(difluoramino)methane was found in the cooling trap.

A liquid product possessing strong oxidizing properties was isolated on extraction of the aqueous reaction mixture. Fractional distillation of this extract yielded a high-boiling compound. The high-boiling liquid (3% yield) was identified as diethyl N,N'-difluoromethylenedicarbamate, $\text{CH}_2(\text{NFCOOC}_2\text{H}_5)_2$, on the basis of its infrared spectrum (Figure 5) and elemental analysis. A weak infrared peak at 2.9μ may be due to a contaminant such as diethyl fluoromethyldicarbamate. Gas chromatographic purification could not be used because of the high boiling point of the material. A preliminary proton NMR spectrum (nuclear magnetic resonance) agreed well with the proposed structure.

The major component of the lower-boiling fraction was separated by gas chromatography and, on the basis of infrared spectrum (Figure 6) and elemental analysis, the compound was tentatively identified as ethyl difluoraminoethylcarbamate, $\text{NF}_2\text{CH}_2\text{NHCOOC}_2\text{H}_5$. The analytical results would also agree with the isomeric structure, $\text{NHFC}_2\text{H}_4\text{NFCOOC}_2\text{H}_5$. NMR spectroscopy will be used to differentiate between these structures.

*Aerojet-General Report 2099 (Annual Summary), November 1961, p. 26 (Confidential).

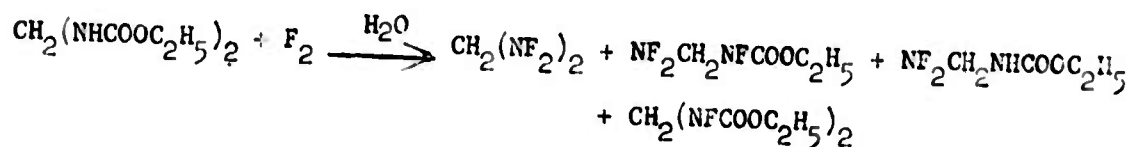
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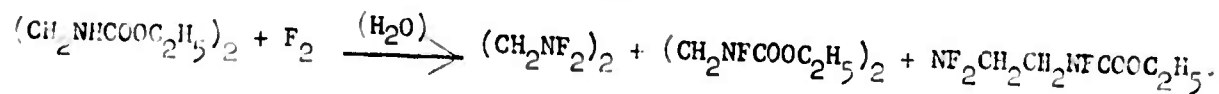
Another component (5 to 10%) of the low-boiling mixture was separated by gas chromatography, and on the basis of its infrared spectrum and elemental analysis the material was tentatively identified as ethyl N-difluoraminoethyl-N-fluorocarbamate, $\text{NF}_2\text{CH}_2\text{NFCOOC}_2\text{H}_5$. The elemental analysis was not completely satisfactory, and additional work is in progress to secure a sample of higher purity.

The fluorination of aqueous diethyl methylenedicarbamate may be tentatively formulated as follows:



The fluorination of diethyl ethylenedicarbamate was carried out under similar reaction conditions to those used for the fluorination of the methylene analogue. The fluorination was again arbitrarily interrupted at a 3 to 1 molar ratio of fluorine to substrate. Traces of 1,2-bis(difluoroamino)ethane were obtained. A high-boiling component present in the mixture of products extracted from the aqueous fluorination mixture was separated by fractional distillation. This compound, isolated in 4% yield, was identified as diethyl N,N'-difluoroethylenedicarbamate, $(\text{CH}_2\text{NFCOOC}_2\text{H}_5)_2$, on the basis of its infrared spectrum (Figure 7) and elemental analysis. Despite an acceptable elemental analysis, the presence of a weak absorption of (2.9 μ) in the infrared spectrum of the compound suggests that the compound was somewhat impure.

A lower-boiling fraction contained several components, most of them only in trace amounts. The major component of this mixture was separated by gas chromatography and, on the basis of its infrared spectrum (Figure 8) and elemental analysis, the compound was identified as ethyl β -difluoroaminoethylfluorocarbamate, $\text{NF}_2\text{CH}_2\text{CH}_2\text{NFCOOC}_2\text{H}_5$. The yield of this material was about 30%. The fluorination of aqueous diethyl ethylenedicarbamate is represented by the following equation:



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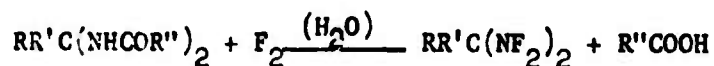
II Technical Discussion, B (cont.)

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It is interesting that while $\text{NF}_2\text{CH}_2\text{NHCOOC}_2\text{H}_5$ was the main reaction product in the fluorination of diethyl methylenedicarbamate, the fluorination of the ethylene analogue gave mainly $\text{NF}_2\text{CH}_2\text{CH}_2\text{NFCOOC}_2\text{H}_5$. In the case of $\text{NF}_2\text{CH}_2\text{NHCOOC}_2\text{H}_5$, the difluoramino group apparently deactivates the NH toward further fluorination. The difluoramino group in $\text{NF}_2\text{CH}_2\text{CH}_2\text{NHCOOC}_2\text{H}_5$, on the other hand, being one carbon further removed from the NH, has less effect on the activity of the NH.

b. Fluorination of Methylenediamides

It has been shown that the fluorination of N-methylamides gives methyldifluoramine in high yields.* Geminal diamides are readily available and the fluorination was extended to these compounds with the objective of synthesizing the corresponding gem-difluoramino derivatives:



Methylenediacetamide was fluorinated in aqueous solution until from 4 to 5 moles of fluorine per mole of diamide were consumed. Only a small amount of impure bis(difluoramino)methane was isolated in the cooling trap.

Workers at Rohm & Haas Co. have reported obtaining bis(difluoramino)methane from the fluorination of aqueous methylenediformamide.** We have attempted this reaction using reaction conditions similar to those used for the fluorination of the diacetamide derivative. As was the case with the latter, only very small amounts of bis(difluoramino)methane were isolated. No study of reaction conditions with a view to improving the yield of $\text{CH}_2(\text{NF}_2)_2$ has yet been made.

c. Fluorination of Allyl- and Arylureas

Fluorination of arylureas has been derived previously.*** N,N-Difluorourea has been identified as one product of these reactions. A volatile

* Aerojet-General Report 2099, p. 21.

** Private communication from Dr. J. P. Freeman, Rohm & Haas Co., to Dr. N. W. Thomas, Aerojet-General Corporation.

*** Aerojet-General Report 2099 (Annual Summary), November 1961, p. 19.

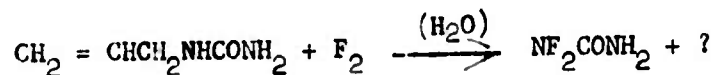
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liquid, b.p. 24°C, was also isolated, which has now been identified as Freon-11 (FCCL₃). This material was a propellant for the Aerosol antifoam agent used to prevent the foaming of the aqueous solution during fluorination.

The fluorination of aqueous allylurea also resulted in cleavage of the C-N bond, with the formation of N,N-difluorourea:



Small amounts of solid and liquid products (with strong oxidizers) were also produced, but these materials have not been identified.

d. Fluorination of Cyanoguanidine

One experiment has been carried out in which aqueous cyanoguanidine was fluorinated. Fluorine was readily consumed and a large amount of a brown, water-insoluble solid was produced. This material possesses no oxidizing properties and has not been identified. A small amount of N,N-difluorourea was isolated from the aqueous solution.

2. Experimental

a. Fluorination of Diethyl Methylenedicarbamate

A solution (partial suspension) of 38 g diethyl methylenedicarbamate (0.2 mole) in 650 ml water was fluorinated at 10 to 15°C with a 1-to-4 mixture of fluorine and nitrogen until approximately 15 liters of fluorine gas was passed into the reaction mixture. The reactor was connected in series with -80 and -110°C traps to condense volatile reaction products. At the end of the run each cooling trap contained 0.3 ml of colorless liquid. The material exploded when an attempt was made to obtain a gas sample for infrared analysis. In another similar experiment, however, a gas sample was secured without explosion and the material was identified on the basis of its infrared spectrum as bis(difluoramino)methane contaminated with carbon dioxide and nitrogen oxides.

The aqueous fluorination mixture, containing from 3 to 5 ml of a heavy colorless liquid, was extracted with seven 75-ml portions of methylene chloride. The combined extracts were dried and filtered and the filtrate was

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concentrated to 75 ml. The methylene chloride solution was stirred with solid sodium bicarbonate for 5 min and filtered; the filtrate was concentrated to remove the solvent. The residue, 16.0 g of a pale yellow liquid, was fractionated, but on the basis of gradually increasing boiling point (25 to 50°C/0.1 mm) and refractive index of the distillate, it was found that the lower-boiling mixture, 13 g, could not be separated on distillation. The end fraction of the mixture, 1.5 g, b.p. 85 to 87°C/0.1 to 0.3 mm, n_D^{25} 1.4232, was identified on the basis of its infrared spectrum and elemental analyses as diethyl N,N'-difluoromethylene-dicarbamate, $\text{CH}_2(\text{NFCOOC}_2\text{H}_5)_2$:

Anal. calc'd for $\text{C}_7\text{H}_{12}\text{F}_2\text{N}_2\text{O}_4$: C, 37.17; H, 5.35; N, 12.4; F, 16.8

Found: C, 36.8 ; H, 5.35; N, 12.3; F, 16.3

The low-boiling material (13 g) was submitted for gas chromatographic analysis. The mixture was found to contain many components, most of them present only in traces. The main component of the mixture was found to be present in 80 to 90 % concentration. A sample of this material was separated on a semipreparative gas chromatographic column for infrared and elemental analyses (see paragraph c, below). The infrared spectrum showed the presence of a strong N-H absorption peak. On the basis of infrared and elemental analysis, the ethyl difluoraminoethylcarbamate structure, $\text{NF}_2\text{CH}_2\text{NHCOOC}_2\text{H}_5$, has been assigned to the compound. However, as noted in the discussion, the isomeric structure, $\text{NHFCCH}_2\text{NFCOOC}_2\text{H}_5$, cannot be excluded. The yield was 30% based on the chromatograph peak areas.

Anal. calc'd for $\text{C}_4\text{H}_8\text{F}_2\text{N}_2\text{O}_2$: C, 31.15; H, 5.23; N, 18.18; F, 24.66

Found: C, 31.5 ; H, 5.40; N, 18.1 ; F, 24.1

Another constituent of this mixture was also isolated. A sample of this material, apparently not pure, was analyzed, but the elemental analysis is somewhat off from that calculated for $\text{NF}_2\text{CH}_2\text{NHCOOC}_2\text{H}_5$.

Anal. calc'd for $\text{C}_4\text{H}_7\text{F}_3\text{N}_2\text{O}_2$: C, 27.9; H, 4.10; N, 16.3; F, 33.1

Found: C, 29.3; H, 4.6 ; N, 15.8; F, 28.6

The material showed practically no N-H absorption in the infrared spectrum.

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b. Fluorination of Diethyl Ethylenedicarbamate

A partial solution of 40.5 g diethyl ethylenedicarbamate (0.2 mole) in 650 ml water was fluorinated at 15 to 20°C with elementary fluorine diluted with nitrogen (1:4) until 16 liters of fluorine gas were passed into the reaction mixture. The reactor was converted in series with -80 and -110°C traps to condense volatile reaction products. At the end of the run, each trap contained 0.2 ml of a colorless liquid. These materials were combined, and a sample was submitted for infrared analysis. The infrared spectrum showed the presence of highly contaminated 1,2-bis(difluoramino) ethane.

The aqueous fluorination mixture containing from 5 to 7 ml of a heavy water-insoluble oil was extracted with ten 75-ml portions of methylene chloride. The combined extracts were dried and filtered and the clear filtrate was concentrated to 100 ml. The solution was deacidified by treating it with 5 g of solid sodium bicarbonate. The filtered solution was concentrated to remove the residual solvent. The residue was purified by distillation and gave 14 g of a colorless liquid, b.p. 20 to 35°C/0.1 to 0.3 mm. The distillation residue, 8 to 9 g of viscous dark liquid possessing only weak oxidizing properties, was not investigated in this experiment.

The distillate was redistilled. After the removal of 12 g of liquid, b.p. 20 to 65°C/0.1 mm, there were collected 2 g of colorless liquid, b.p. 76 to 78°C/0.1 mm, n_D^{25} 1.4245. This material was redistilled, b.p. 78 to 79°C/0.1 to 0.3 mm, n_D^{25} 1.4258. On the basis of the infrared spectrum and elementary analysis, the compound was identified as diethyl N,N'-difluoroethylene-dicarbamate, $\text{CH}_2(\text{NFCOOC}_2\text{H}_5)_2$.

Anal. calc'd for $\text{C}_8\text{H}_{14}\text{F}_2\text{N}_2\text{O}_4$: C, 40.0; H, 5.87; N, 11.66; F, 15.22

Found: C, 39.8; H, 5.76; N, 11.80; F, 15.4

The mixture of lower-boiling products (12 g) could not be purified by distillation. The material was submitted for gas chromatographic analysis. It was found that the mixture contained many components, most of them

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present only in traces. One compound, 85 to 90% of the total, was predominant in the mixture. A sample of this material was separated for infrared and elemental analyses on a semipreparative column. On the basis of elemental analyses and the infrared spectrum (no N-H absorption peak), the compound was identified as ethyl difluoraminoethylfluorocarbamate, $\text{NF}_2\text{CH}_2\text{CH}_2\text{NFCOOC}_2\text{H}_5$, yield 30%.

Anal. calc'd for $\text{C}_5\text{H}_9\text{F}_3\text{N}_2\text{O}_2$: C, 32.26; H, 4.87; N, 15.05; F, 30.62

Found: C, 32.5 ; H, 4.82; N, 14.8 ; F, 30.8

c. Analysis of Products from the Fluorination of Diethyl Methylenedicarbamate (I) and Diethyl Ethylenedicarbamate (II) (R. M. Roberts)

Distilled isolates taken from these two fluorinated reaction mixtures were examined by gas chromatography under essentially identical conditions. A $3/8 \times 6$ -in. column of 5% LAC (ethylene glycol-succinate polyester) on Chromosorb was operated at 90°C at a helium flow rate of 200 ml/min. Ten constituents were detected in mixture I and seven in mixture II. From the richer distillation cuts, 85 to 90% of the material was eluted as pure component from I after 9-1/2 min, while a 90-to-95% yield was obtained from II as a lower-boiling eluate in about 7 minutes. These chromatographically pure isolates were liquids at room temperature and could be collected directly into tared capillary tubes without resorting to chilling. When 50- μ l portions of the mixtures were run, only two or three injections were needed to provide ample center cuts for elemental and infrared analysis.

The capillary tubes, initially sealed on one end, then left completely open in most of the component work, were immediately taken for analysis. Pregl microcombustion C-H analysis was performed according to the method described by Strahm.* A notable modification introduced in the Strahm

*R. D. Strahm, in Bulletin of 16th Meeting, JANAF Panel on Analytical Chemistry of Solid Propellants, October 4-6, 1960, pp 45-7

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method was the inclusion of a 15-mm section of MgO between the Ag and the second Co_2O_3 section. This greatly extends the life of the combustion tube by eliminating HF attack on the quartz walls. This addition was largely made at the expense of the first CuO bed, which was shortened to about 30 mm. This did not constitute a compromise, however, since the capillary tube was placed in a ceramic boat and buried in CuO to minimize chances of detonation. At Strahm's verbal suggestion, the ratio of $\text{CuO}:\text{Cr}_2\text{O}_3$ in the mixed bed was also changed from 2:1 to 10:1. Nitrogen was determined by the micro Dumas method outlined in the same reference, but without modification.

Fluorine analysis was performed by the Knallgasflamme or Wickbold technique, in which the volatilized sample undergoes combustion in a hydrogen-oxygen flame contained in an all-quartz system.* A new thorium titration, involving the mixed indicator alizarin-methylene blue was investigated and found to yield superior reproducibility to that of the standard methods.**

d. Fluorination of Methyleneformamide

A solution of 10.2 g methylenediformamide in 350 ml water was fluorinated at 0 to 5°C as described above. Fluorination was continued until 12 liters of fluorine had passed into the reaction mixture. Fluorination was quite sluggish and considerable amounts of unreacted fluorine escaped from the reactor. At the end of the run, the -80 and -110°C traps each contained 0.1 ml of a volatile liquid. This material was identified by its infrared spectrum as bis(difluoramino)methane contaminated with carbon dioxide and other unknown impurities.

e. Fluorination of Allylurea

A solution of 25 g allylurea (0.25 mole) in 1000 ml water was fluorinated at 0 to 5°C with elementary fluorine (diluted with nitrogen, 1:4) until 21 liters of fluorine gas were passed into the reaction mixture. At the

*R. Levy, in Proceedings of the International Symposium on Microchemistry, 1958, Pergamon Press, 1960, p. 112.

**H. Soep, Mededeel Vlaam Chem Ver 21, 49 (1959) (CA 54, 4253, 1960)

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end of the run the pale-yellow reaction mixture contained small amounts of suspended solid. The -80°C trap converted in series with reaction flask contained 0.2 ml of a colorless liquid.

The aqueous mixture was extracted with seven 50-ml portions of diethyl ether. The solid dissolved slowly. The ether solution was dried, filtered and concentrated to remove the solvent. The viscous residue was distilled to give from 1 to 2 g of colorless liquid, b.p. $40^{\circ}\text{C}/0.1$ to 0.3 mm (partial sublimation), which solidified to a white solid. This material was identified as N,N-difluorourea by comparing its infrared spectrum with that of an authentic sample.

The distillation residue, from 1 to 2 g of a viscous brown oil, solidified on washing with methylene chloride. This material was not identified.

f. Fluorination of Cyanoguanidine

A solution of 42 g cyanoguanidine (0.5 moles) in 650 ml water was fluorinated at 10 to 15°C with elementary fluorine (diluted with nitrogen 1:4) until 22 liters of fluorine gas had passed into the reaction mixture. A liquid (0.2 ml) which accumulated in the -110°C trap was lost in manipulation.

The aqueous reaction mixture, containing large amounts of a brown solid, was filtered, and the solid material washed first with water, then with ethanol and ether. The solid, b.p. $> 300^{\circ}\text{C}$ (no oxidizing properties), amounted to 8 grams.

The aqueous filtrate was extracted with seven 70-ml portions of diethyl ether, and the combined extracts were dried, filtered and concentrated. The semi-solid residue was purified by distillation at 50°C and 0.1 mm pressure to give 1 g of white crystalline solid, which was identified by its infrared spectrum as N,N-difluorourea.

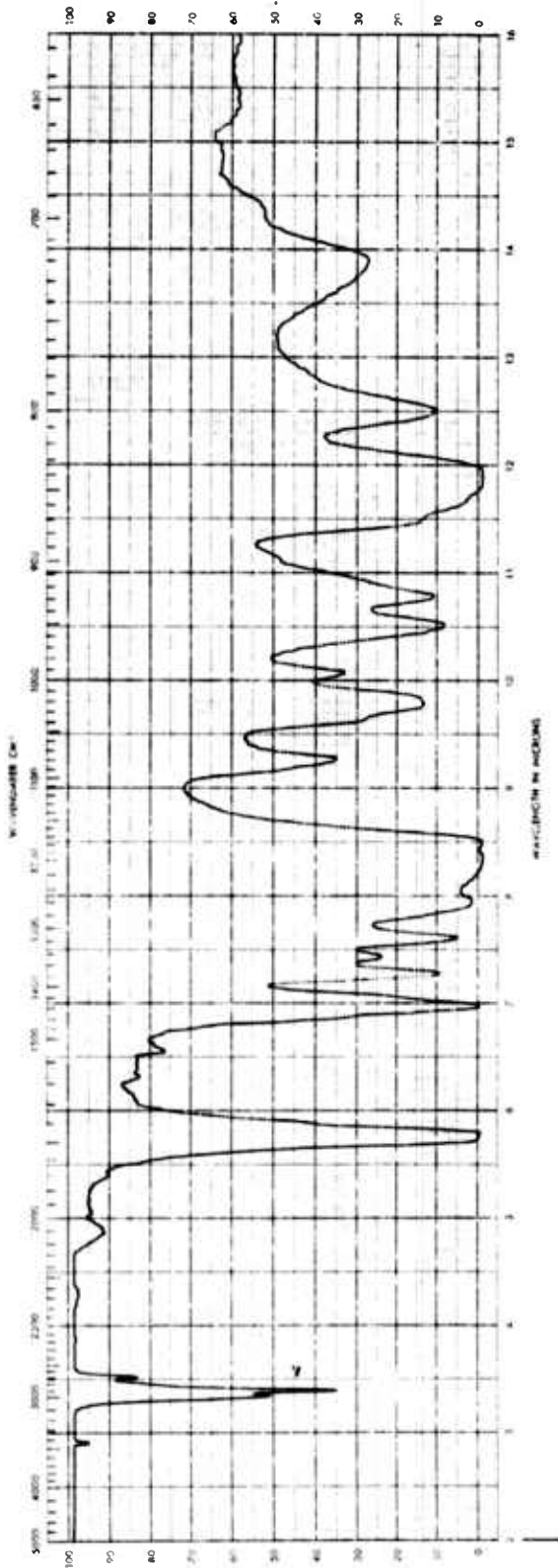


Figure 1. Methyl β -Difluoraminopropionate

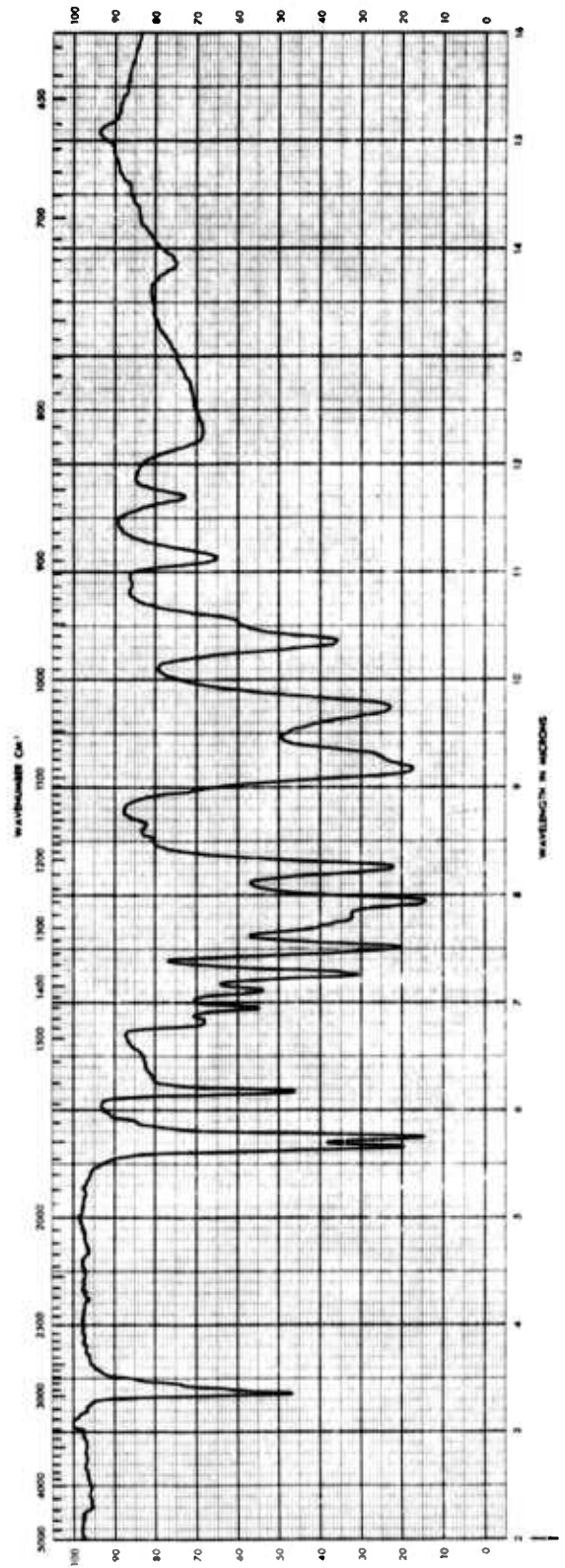


Figure 2. Product from Ethoxyacetylene

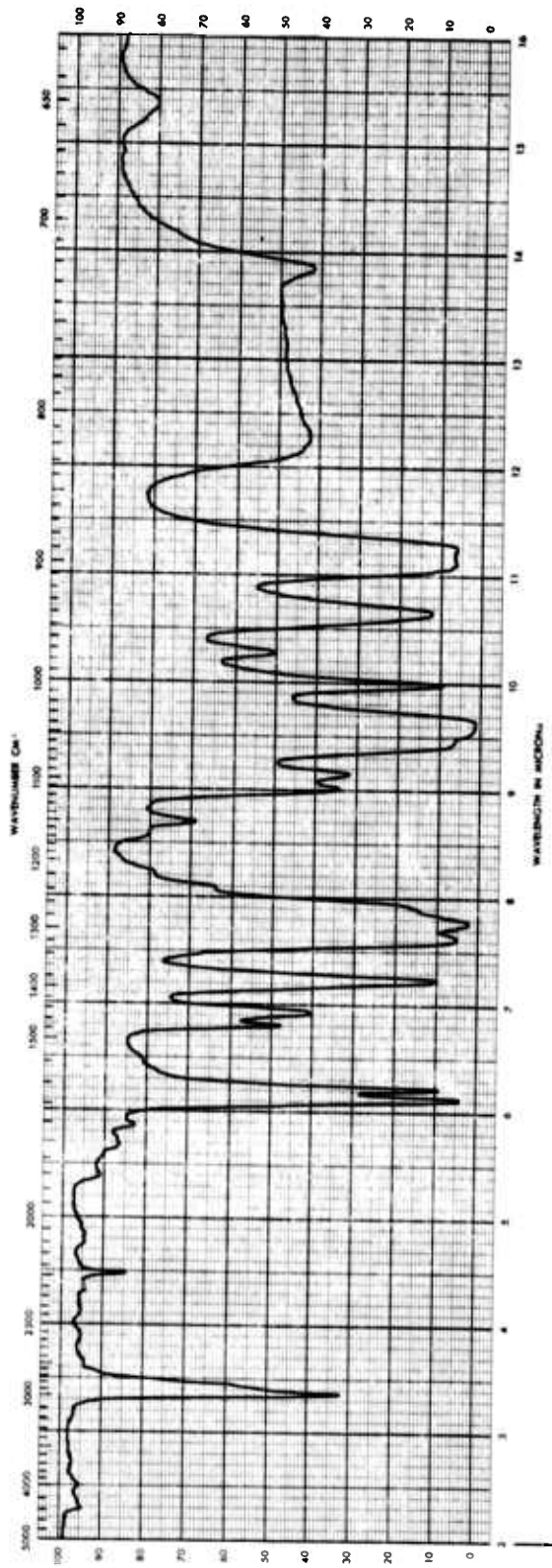


Figure 3. Product from Ethoxyacetylene

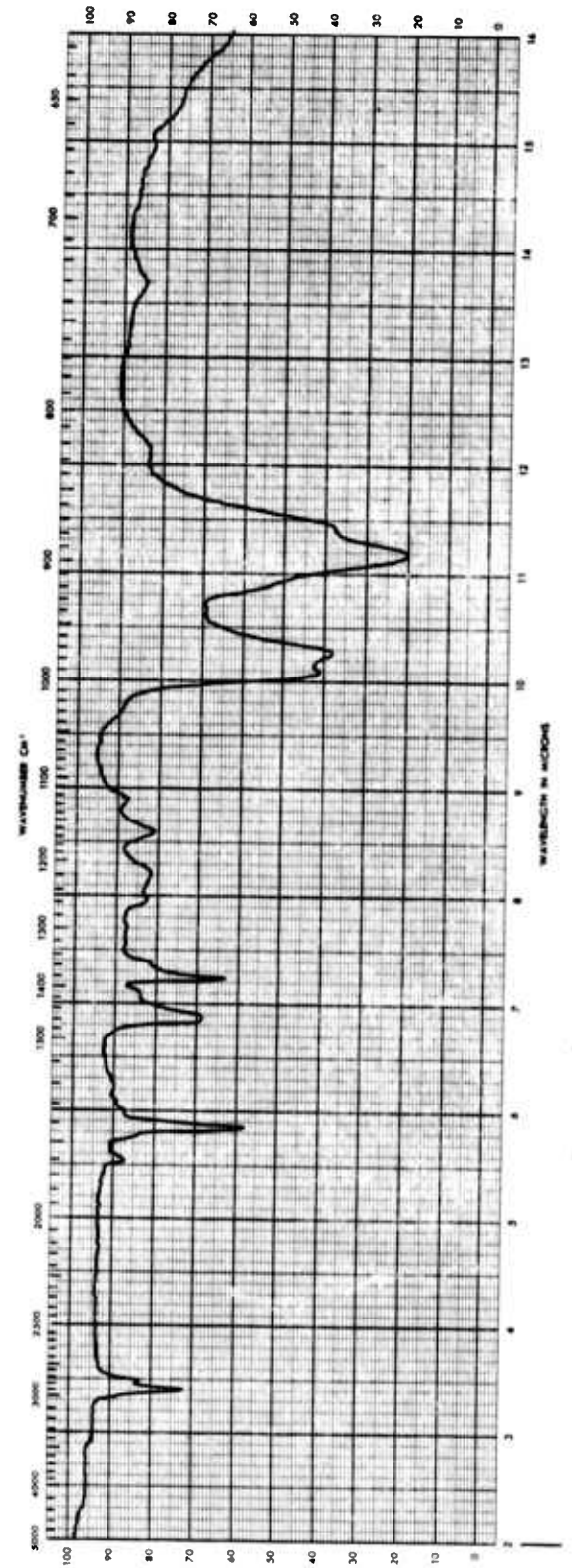


Figure 4. 2,2,7,7-tetrakis(Difluoramino)octane

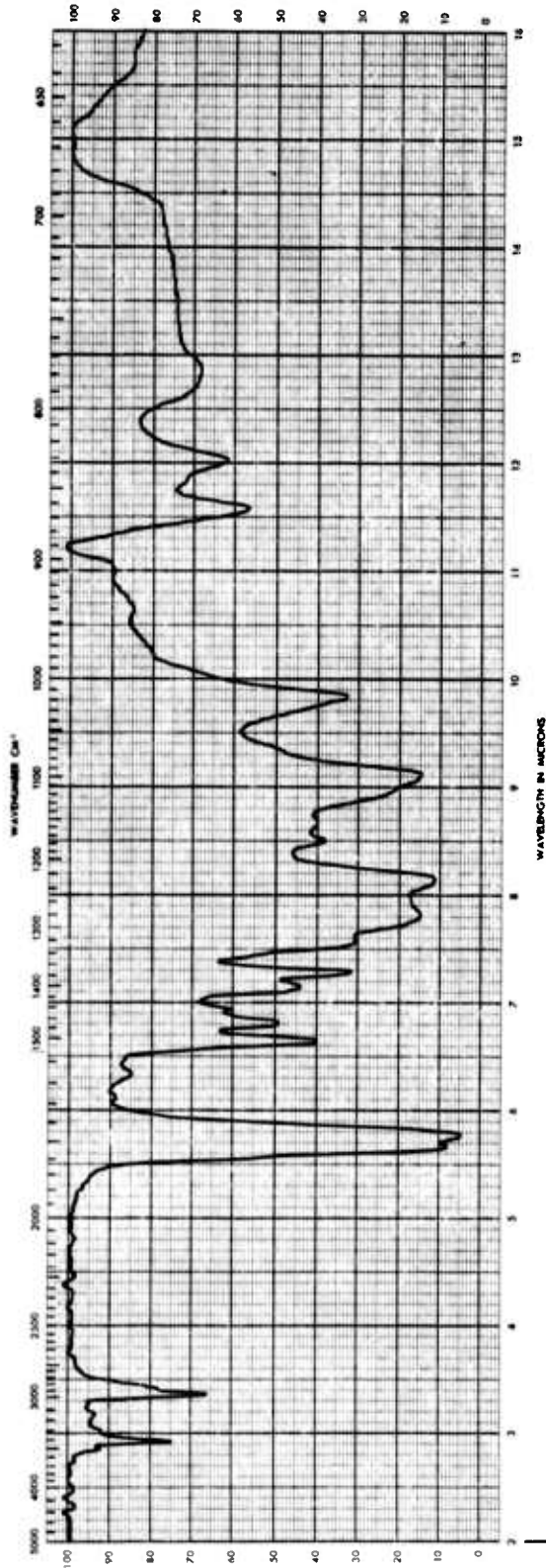


Figure 5. Diethyl N,N'-Difluoromethylenedicarbamate

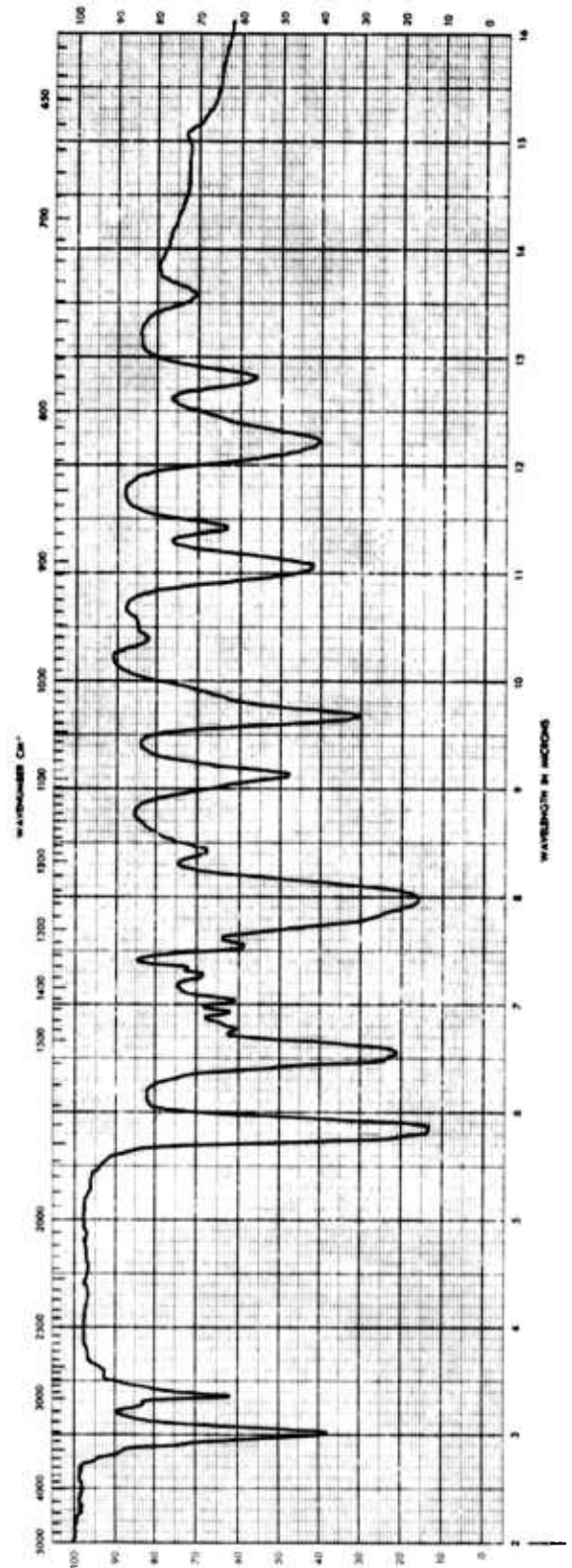


Figure 6. Ethyl Difluoraminomethylcarbamate

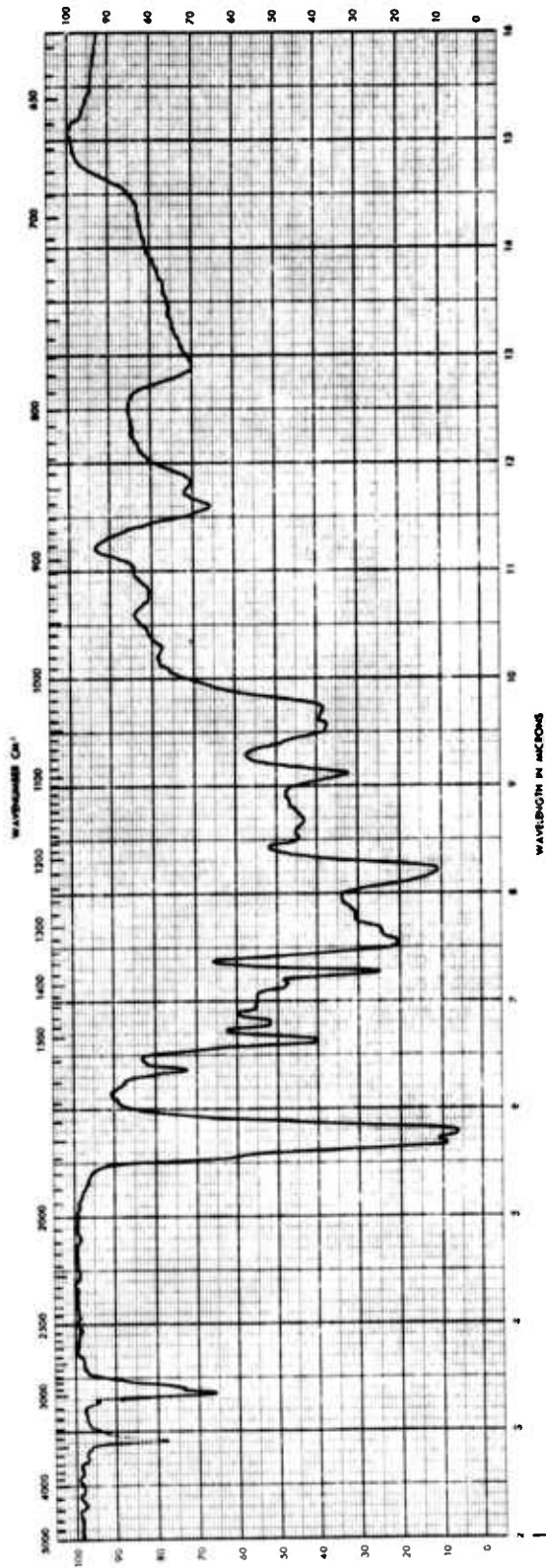


Figure 7. Diethyl N,N'-Difluoroethylenedicarbamate

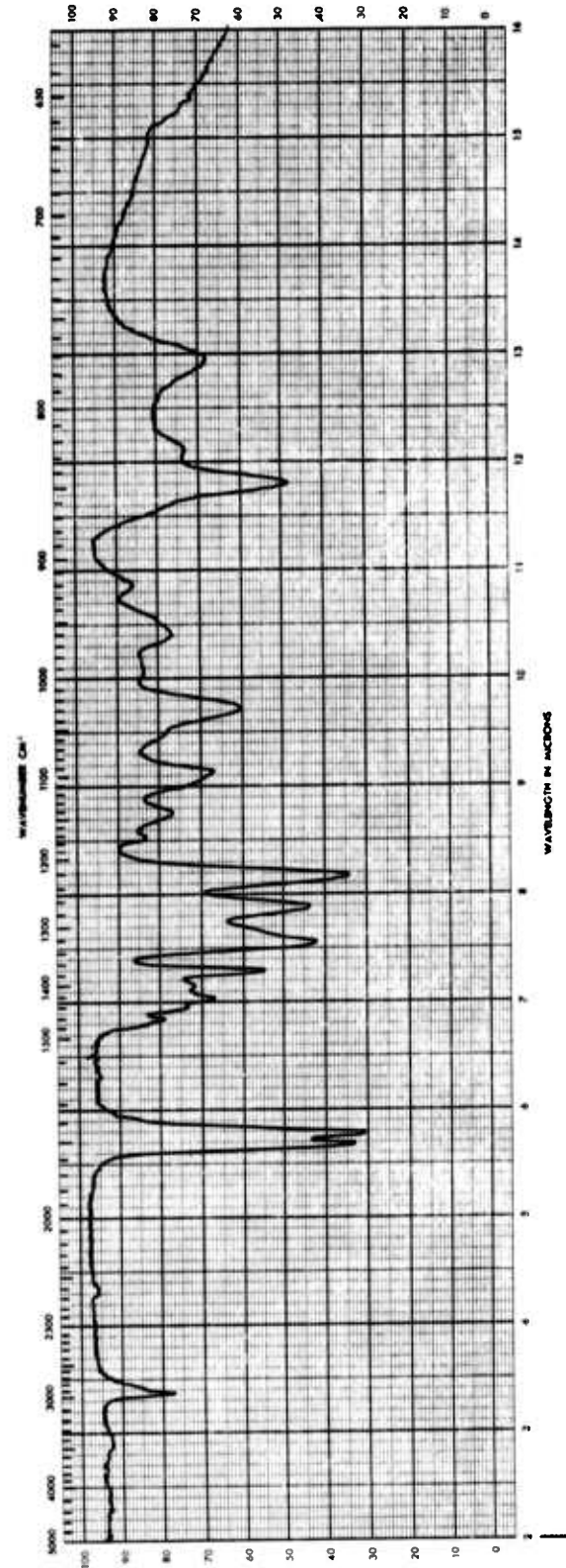


Figure 8. Ethyl beta-Difluoroaminoethylfluorocarbamate

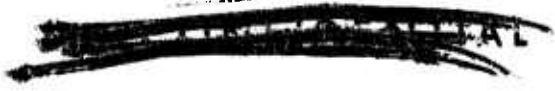
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