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RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT TO

OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

OCTOBER 1966

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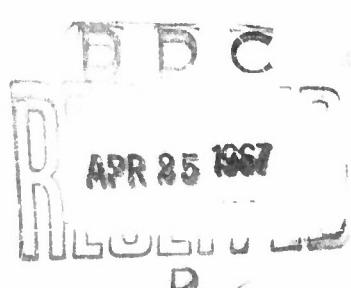
CHEMICAL AND STRUCTURAL PRODUCTS DIVISION

AEROJET-GENERAL CORPORATION

AZUSA, CALIFORNIA

(0235)

United States Patent Office Secrecy Order

October 1966

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

By

K. Baum, V. Grakauskas, L. A. Maucieri

Analytical Support: K. Inouye

A Report to

OFFICE OF NAVAL RESEARCH
and
ADVANCED RESEARCH PROJECTS AGENCY

Von Karman Center

AEROJET-GENERAL CORPORATION

A Subsidiary of The General Tire & Rubber Company

ABSTRACT

Reactions of diazonium salts with N-fluorocarbamates in the presence of mild bases gave azides and alkyl fluoroformate. Reactions of diazonium salts with difluoramine gave aromatic azides with fluorine introduced into the ortho or para position. When all ortho and para positions were blocked by substituents, aromatic azides were formed, and fluorine was apparently consumed by reaction with difluoramine. Reduction of diazonium groups also occurred, apparently favored by electron-withdrawing substituents.

The reaction 2,5,8-triketononane with difluoramine and fuming sulfuric acid gave 2-methyl-2,5-bis(difluoramino)-5-$[\gamma,\gamma$-bis(difluoramino)butyl$]$ tetrahydrofuran.

No reaction took place between picryl chloride and neat liquid difluoramine in 73 hours. The addition of pyridine gave no fluorine-containing products.

The reaction ethyl diazoacetate with difluoramine and sulfuric acid gave ethyl difluoroaminoacetate. Ethyl azodicarboxylate did not react with difluoramine, and nitroacetaldehyde phenylhydrazone gave only tars. 2-Phenylazo-2-nitropropane was converted to 2-phenylazo-2-difluoraminopropane.

A simplified process for the preparation of high-purity fluoroammonium perchlorate (SAP) was developed, based on the reaction between isopropyl N-fluorocarbamate and anhydrous perchloric acid. Yields were almost quantitative.

Alkylation and Mannich condensation reactions of 2,2-dinitro-2-fluoroethanol were briefly investigated. 2,2-Dinitro-2-fluoroethyl methyl and 2,2-dinitro-2-fluoroethyl allyl ethers were obtained on treatment of alkaline solutions of 2,2-dinitro-2-fluoroethanol with dimethyl sulfate and allyl bromide, respectively.

CONTRACT FULFILLMENT STATEMENT

This annual summary technical report is submitted in partial fulfillment of the contract and covers the period from 1 October 1965 through 30 September 1966.

AEROJET-GENERAL CORPORATION

W. P. Knight, Manager
Applied Chemistry Department

L. R. Rapp, Manager
Chemical and Structural Products Division

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I.   INTRODUCTION

This report summarizes the research carried out under Contract Nonr 2655(00) during the period 1 October 1965 through 30 September 1966. Experimental details are included only for the work of 1 July 1966 through 30 September 1966, since the work of 1 October 1965 through 30 June 1966 was covered in Aerojet Quarterly Reports No. 0235-01-24 and 0235-01-25/26. 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 Reports No. 1163, 1318, 1509, 1685, 1877, 2099, 2381, 2730, 2945, and 3132.

During the past year, research was continued on reactions of difluoramine with the objective of developing general methods for preparing energetic compounds, and obtaining a more thorough understanding of the reactions involved. Work was continued on the preparation and characterization of fluorammonium perchlorate, and a process suitable for the production of pound quantities was developed. Samples of this material were shipped to other laboratories for evaluation of its potential as a solid oxidizer. Some reactions of fluorodinitroethanol were also examined with the objective of preparing mixed nitro-NF compounds.

II.   REACTIONS OF DIFLUORAMINE (K. Baum)

A.   DISCUSSION

1.   Diazonium Salts

The synthesis of aromatic difluoramino compounds by the fluorination of electronegatively substituted anilines in anhydrous hydrogen fluoride has recently been reported.[*] With the objective of developing an alternate and perhaps more versatile route to aromatic difluoramines, the reaction of diazonium salts with difluoramine was investigated.

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[*] Synthesis of High Energy Oxidizers, Stanford Research Institute Quarterly Report No. 12, 30 October 1965 (Confidential).

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Most reactions of diazonium salts fall within the classes of (a) coupling, with or without loss of nitrogen, and (b) reduction, typified by reactions with azide, aniline, and hypophosphorous acid, as follows:[*]

$$ArN_2^{\oplus} + N_3^{\ominus} \longrightarrow ArN_3 + N_2$$

$$ArN_2^{\oplus} + NH_2\text{-}C_6H_5 \longrightarrow Ar\text{-}N=N\text{-}NH\text{-}C_6H_5$$

$$ArN_2^{\oplus} + H_3PO_2 \longrightarrow ArH$$
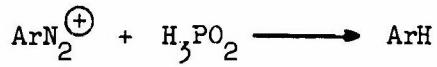
By these routes difluoramine could be expected to yield aromatic difluoramines, difluorotriazenes, or aromatic hydrocarbons.

Preliminary studies were made with isopropyl N-fluorocarbamate as a model compound for difluoramine. No reaction took place when isopropyl N-fluorocarbamate was added to a suspension of benzenediazonium fluoborate in methylene chloride. The addition of pyridine, however, resulted in the formation of pyridine fluoborate, phenyl azide, and isopropyl fluoroformate. The latter compound was identified by elemental analysis and by comparison with previously reported spectral data.[**]

The most plausible mechanism for the formation of these products involves diazonium coupling to the carbamate to give 1-phenyl-3-fluoro-3-carboisopropoxytriazene, followed by fluorine migration to carbon and C-N cleavage:

$$C_6H_5\text{-}N_2^{\oplus} BF_4^{\ominus} + HNF\text{-}CO_2\text{-}\underline{i}Pr + C_5H_5N \longrightarrow C_6H_5\text{-}N=N\text{-}NF\text{-}CO_2\text{-}\underline{i}Pr + C_5H_5N\cdot HBF_4$$

$$C_6H_5\text{-}N=N\text{-}\overset{\overset{\displaystyle F}{|}}{N}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\underline{i}Pr \longrightarrow C_6H_5N_3 + F\underset{\underset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\underline{i}Pr$$

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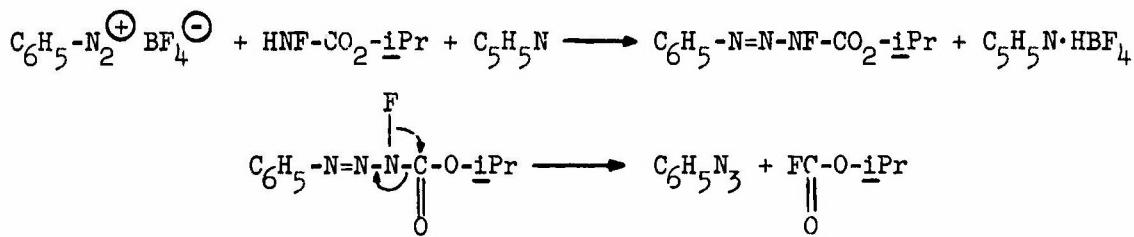
[*] For a review, see P. A. S. Smith, <u>Open-Chain Nitrogen Compounds</u>, Vol. II, New York, W. A. Benjamin, Inc., 1966.

[**] K. O. Christi and A. E. Pavlath, <u>J. Org. Chem.</u>, <u>30</u>, 1639 (1965).

It was subsequently found that potassium fluoride could be used instead of pyridine as a scavenger for fluoboric acid. High yields of the corresponding azides (known compounds)[*] were obtained from o-nitrobenzene-diazonium fluoborate, m-nitrobenzenediazonium fluoborate, and p-nitrobenzene-diazonium fluoborate. Methoxybenzenediazonium salts also gave azides, evidenced by infrared peaks at 4.7 microns, but the products (which were unstable) were not characterized fully.

The reaction of benzenediazonium fluoborate with difluoramine was investigated initially with a large excess of liquid difluoramine at its boiling point. The diazonium salt was very soluble in difluoramine but was recovered quantitatively when the difluoramine was removed. Reaction occurred when pyridine or potassium fluoride was added to remove fluoboric acid.

The infrared spectrum of the product soluble in methylene chloride showed strong azide absorption at 4.7 μ. The F^{19} nuclear-magnetic-resonance (NMR) spectrum contained peaks at 118.1 and 127.5 ϕ, which were shown to be due to p-fluorophenyl azide, and o-fluorophenyl azide, respectively. The compounds were synthesized independently by the nitrosation of the corresponding fluorophenylhydrazines, and the F^{19} NMR spectra showed peaks at these positions with the same profiles. m-Fluorophenyl azide was also synthesized, and was shown not to be present in the difluoramine reaction product. A 1:1:1 triplet at -32.5 ϕ and a broad singlet at -26.2 ϕ were found in several runs, but were absent in other runs under essentially the same conditions. These peaks are in the NF region, but structural assignments cannot be made at present. Benzene was also formed in variable amounts.

Although potassium fluoride was effective in promoting this reaction, sodium fluoride gave no reaction, probably because of the much greater solubility of sodium fluoborate. On the other hand, the addition of a trace of cesium fluoride to the difluoramine solution of the diazonium salt resulted in a detonation. When methylene chloride was used as a diluent, a fume-off took place. A sodium carboxylate type of ion-exchange resin (Bio-Rex 70) also failed to promote the reaction.

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[*] Zincke and Schwarz, Ann., 307, 35 (1899); Noelting, Grandmougin, and Michel, Ber., 25, 3338 (1892); and H. Rupe and K. V. Majewski, Ber., 33, 3408 (1900).

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       o-Fluorophenyl azide and p-fluorophenyl azide could be formed from the simple coupling product, 1-phenyl-3,3-difluorotriazene, by loss of fluoride ion, addition of fluoride to the electrophilic carbons of the resonance-stabilized cation, and loss of HF. This mechanism is consistent with the absence of the meta isomer in the product:
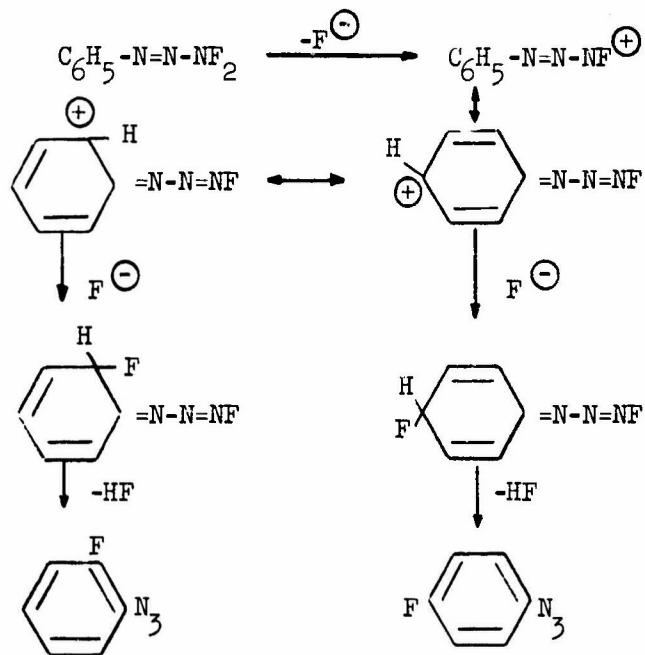
       The benzene was probably formed by a homolytic path, as is usually the case in diazonium-salt reductions.[*] The aryl or diazoaryl radical formed in the cleavage of the triazene could abstract a hydrogen from difluoramine to give the stable difluoramino radical:

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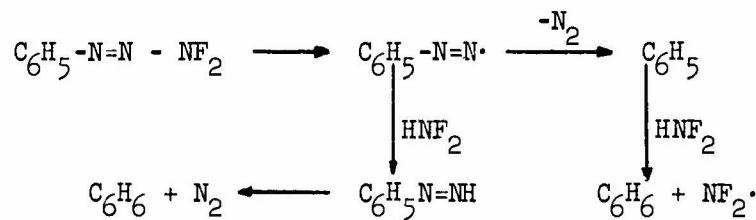
[*] P. A. S. Smith, op. cit.

II Reactions of Difluoramine, A (cont.)   Report No. 3299

        Reactions of other diazonium salts with difluoramine were also studied. Thus, o-, p-, and m-nitrobenzenediazonium fluoborates gave mainly nitrobenzene, but in each case fluoroazides appeared to be formed in small amounts since the infrared spectra had 4.7-μ peaks and the F^{19} NMR spectra contained weak aromatic CF signals. In the case of the p-nitrobenzenediazonium reaction, there was a small F^{19} NMR doublet at -33.7 ϕ (J = 116 cps) with each leg showing AB-type splitting. p-Methoxybenzenediazonium fluoborate gave an azide, but no anisole was detected.

        Picramide was diazotized in sulfuric-acid solution,[*] and the solution was treated with difluoramine. A high yield of 1,3,5-trinitrobenzene was isolated. On the other hand, a sulfuric-acid solution of diazotized 2,6-dinitroaniline gave a product with an azide band in the infrared, but with an elemental analysis that could not be reconciled with any such structure.

        In general, it appears that electron-withdrawing substituents favor reduction, and electron-donating substituents favor azide formation. These results are consistent with the above mechanisms. Electron-withdrawing substituents would make ionization of fluoride in the triazene more difficult, allowing the triazene to survive long enough to decompose by a free-radical path.

        A diazonium salt with no electronegative substituents, but with its ortho and para positions blocked - i.e., 2,4,6-trimethylbenzenediazonium fluoborate - was reacted with difluoramine and potassium fluoride. The product was 2,4,6-trimethylphenyl azide and a trace of mesitylene. The ionization of fluoride from the coupling product in this case should be relatively facile because the cation is stabilized by three methyl groups. If fluoride adds to the ring, however, aromatization cannot occur, so the addition would be reversible. The cation could lose $F^{\oplus}$ by fluorinating difluoramine to yield 2,4,6-trimethylphenyl azide:

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[*]L. Blangey, _Helv. Chim. Acta_, 8, 782 (1925).
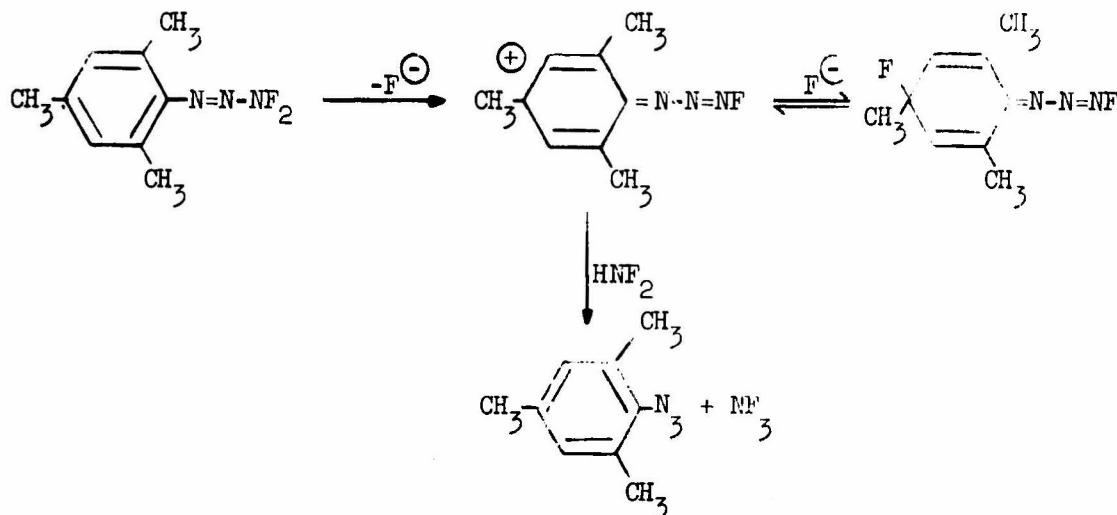
2.   Alkylation

The reaction of acetonylacetone with refluxing difluoramine in sulfuric acid has been shown to yield 2,5-dimethyl-2,5-bis(difluoramino)tetra-hydrofuran.[*] Under more forcing conditions, this cyclic ether was cleaved and difluoraminated to give 2,2,5,5-tetrakis(difluoramino)hexane.[**] Although this product was too volatile for use in solid propellants, structurally similar products derived from polyketones might be usable.

The syntheses of 2,5,8-triketononane and 2,5,8,11-tetra-ketododecane have been reported, using the hydrolysis of 2-methyl-4-(γ-keto-butyl)furan and 2,4-bis(γ-ketobutyl)furan, respectively.[***] The reaction of 2,5,8-triketononane with difluoramine was attempted under a variety of experimental conditions, using 20% fuming sulfuric acid as the catalyst, but the only product isolated was 2-methyl-2,5-bis(difluoramino)-5-$\left[\gamma,\gamma\text{-bis(difluoramino)-butyl}\right]$tetra-hydrofuran.[****] The mechanism of this reaction probably consists of an initial protonation of a carbonyl oxygen, followed by cyclization, and finally, reaction of the pendant carbonyl:

---

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

[**]Aerojet-General Report 0235-01-14, June 1962, p. 2 (Confidential).

[***]K. Alder and C. Schmidt, Ber., 76, 183 (1943).

[****]Aerojet-General Report 0235-01-24, October-December 1965, p. 1 (Confidential).
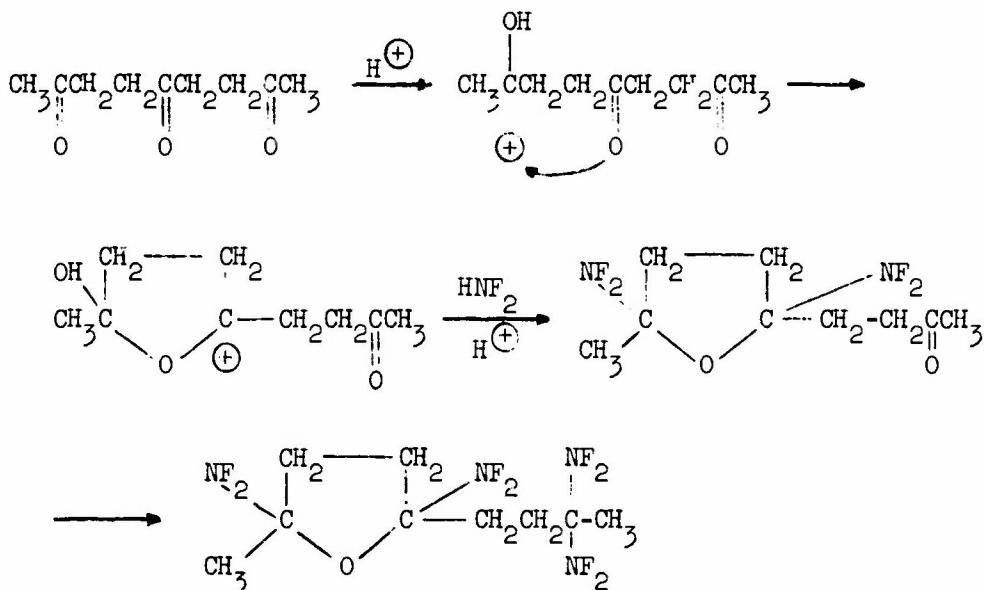
The addition of two moles of bromine to alkynes was reported in the earlier literature.[*] Adducts of this type would be interesting starting materials for difluoramine reactions, potentially yielding compounds with four difluoramino groups on two carbon atoms. In the present work,[**] the addition of two moles of bromine to 3-hexyne in carbon tetrachloride at $10^{o}C$ gave as the major product, 3,4,4-tribromo-2-hexene, which was identified by elemental analysis. The NMR spectrum of the material confirmed this structure, but indicated that an isomeric contaminant was present. The tribromohexene was apparently formed from 3,3,4,4-tetrabromohexane by dehydrobromination.
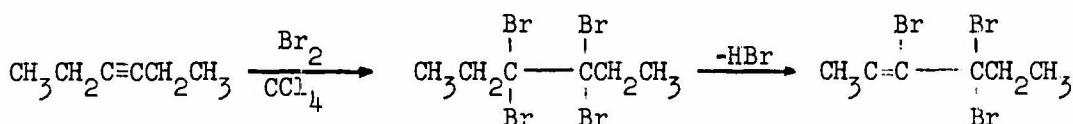
The reaction of the crude 3,4,4-tribromo-2-hexene with difluoramine in fuming sulfuric acid gave a high-boiling liquid product. Its infrared spectrum contained a strong carbonyl group, and its proton NMR spectrum

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[*] Van Risseghem, Compt. Rend., 158, 1697 (1913).

[**] Aerojet-General Report 0235-01-24, October-December 1965, p. 41 (Confidential).

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indicated an unsplit ethyl group and a CH_3CHNF_2 group. The F^{19} spectrum showed the above NF_2 group and an additional one, probably attached to an asymmetrical center. These structural features could not be reconciled to any formula that corresponds to the observed elemental analysis.

Attempts were also made to find a general route to β,β-bis(difluoramino)-gem-dinitro compounds. Halogenation of the acidic hydrogens of Michael addition products of nitroolefins, and 1,1-dinitro-alkanes should give suitable intermediates for difluoramine reactions.

$$RC(NO_2)_2H + R'C(NO_2)=CH_2 \longrightarrow R'\overset{\overset{H}{|}}{\underset{\underset{NO_2}{|}}{C}}-CH_2C(NO_2)_2R$$

$$\overset{X_2}{\longrightarrow} R'\overset{\overset{X}{|}}{\underset{\underset{NO_2}{|}}{C}}-CH_2C(NO_2)_2R \xrightarrow[H^{\oplus}]{HNF_2} R\overset{\overset{NF_2}{|}}{\underset{\underset{NF_2}{|}}{C}}CH_2C(NO_2)_2R$$
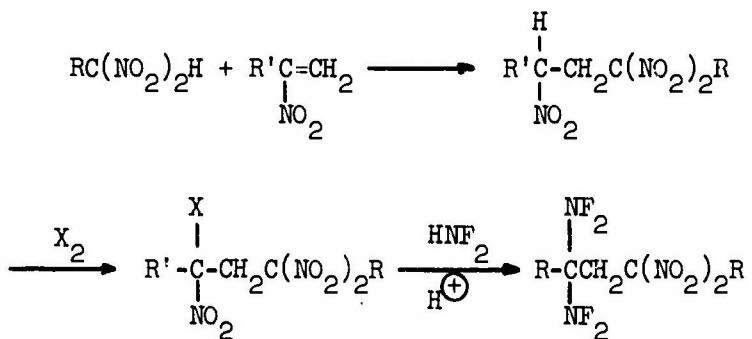
Preliminary studies were made using 2,2,4-trinitrohexane as the starting material, prepared by the in situ reaction of 1,1-dinitroethane, 2-nitrobutyl acetate, and sodium acetate buffer.[*] The reaction of 2,2,4-trinitrohexane with a large excess of aqueous sodium hypochlorite solution at room temperature gave two fractions, shown to be 1,3,3,4-tetrachloro-2,2,4-trinitrohexane and an equimolar mixture of 2,2,4-trinitro-4-chlorohexane and 2,2-dinitro-4-chloro-3-hexene, respectively. The reaction was difficult to reproduce, and a sufficient quantity of the latter mixture was not obtained for difluoramination studies. The initial chlorination site is most likely the acidic hydrogen atom adjacent to the single nitro group. The central methylene group of this product is apparently activated sufficiently by the nitro groups to form an anion, which can then undergo chlorination or loss of nitrite. A second chlorine should be introduced at this site more rapidly than the first.

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[*] H. Feuer and R. Miller, J. Org. Chem., 26, 1348 (1961).
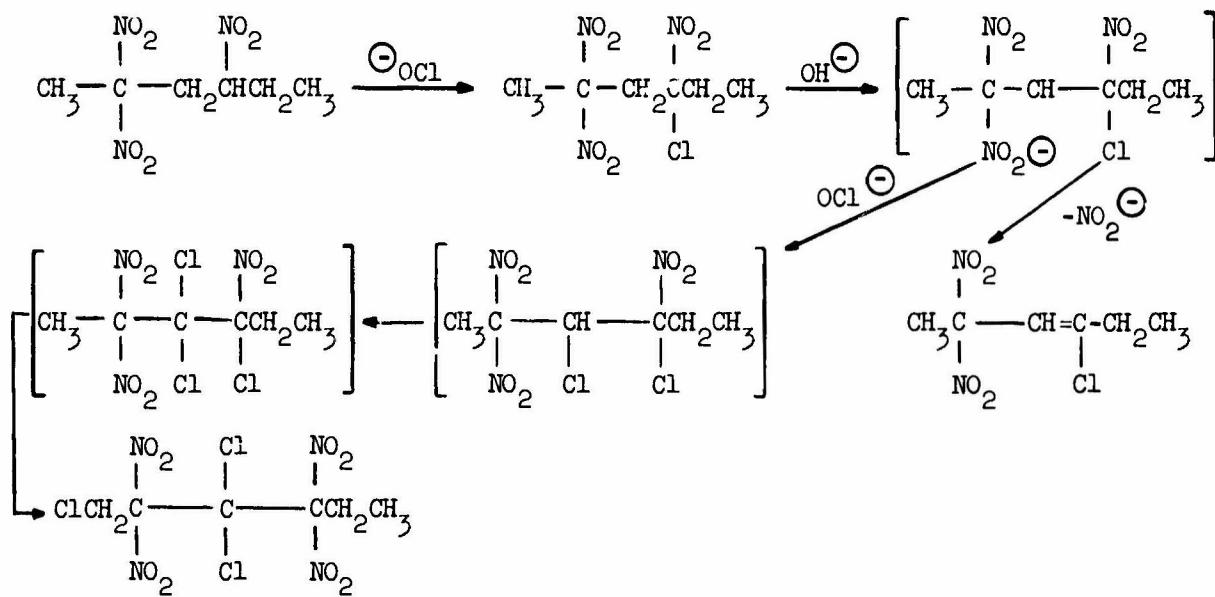
This reaction was repeated using a shorter reaction period (0.5 hour instead of 4 hours), but only the starting material was isolated. Several attempts to brominate 2,2,4-trinitrohexane under similar conditions gave either no reaction or mixtures of products which could not be separated readily.

Since the chlorine in picryl chloride is replaced easily by a variety of reagents, the reaction with difluoramine appeared attractive as an alternative synthesis of trinitrophenyldifluoramine. No reaction took place between liquid difluoramine and picryl chloride at ambient temperature during a 73-hour period, however. The addition of pyridine to picryl chloride and refluxing difluoramine gave a red solid which melted over a broad range and contained no fluorine.
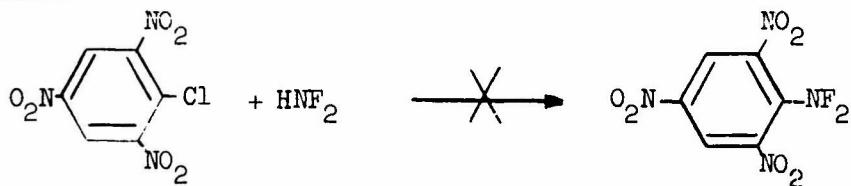
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3.   Miscellaneous Nitrogen Compounds

Active hydrogen species, such as alcohols and mercaptans, are
known to add to the azo linkage of ethyl azodicarboxylate.[*]

$$ROH + EtOOC-N = N-COOEt \longrightarrow EtOOC-\overset{\overset{\displaystyle OR}{|}}{N}-NHCOOEt$$
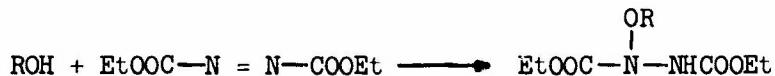
This type of addition with difluoramine was attempted with the objective of
preparing difluorodicarbethoxytriazene. No reaction took place between liquid
difluoramine and ethyl azodicarboxylate, and the latter was recovered quantitatively.

Ethyl diazoacetate was also treated with liquid difluoramine.
Without the use of catalysts, no reaction took place and with the addition of
potassium fluoride the same result was obtained. However, when sulfuric acid
was added to a mixture of ethyl diazoacetate and difluoramine, ethyl difluoramino-
acetate was formed and was identified by its infrared and NMR spectra. This
compound was prepared previously by another method.[**] The product was probably
formed by the alkylation of difluoramine by the carbonium ion resulting from
protonation of the diazo compound and nitrogen loss.

$$EtOOCCHN_2 \xrightarrow{H\oplus} EtOOCCH_2N_2\oplus$$

$$\xrightarrow{-N_2} EtOOCCH_2\oplus \xrightarrow{HNF_2} EtOOCCH_2NF_2$$
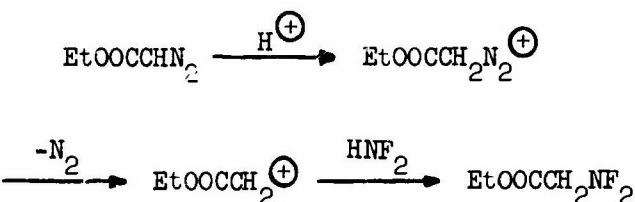
2-Phenylazo-2-nitropropane is prepared easily by the diazonium
coupling reaction of 2-nitropropane.[***] It was hoped that the phenyl azo group
would be displaced in a reaction with difluoramine and sulfuric acid. Instead,
the nitro group was removed to give 2-phenylazo-2-difluoraminopropane, identified
by elemental analysis, NMR, and infrared spectra (Figure 1).

---

[*] O. Diels and C. Wulff, Ann., 437, 309 (1924).

[**] Aerojet-General Report 2730, October 1963, p. 34 (Confidential).

[***] C. F. Feasley and E. F. Degering, J. Org. Chem., 8, 12 (1943).

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$$C_6H_5{-}N = N{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}NO_2 \quad \xrightarrow[{-HNO_2}]{H^{\oplus}} \quad C_6H_5{-}N = N{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}^{\oplus}$$

$$\Big\downarrow \; HNF_2$$

$$C_6H_5{-}N = N{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}NF_2$$
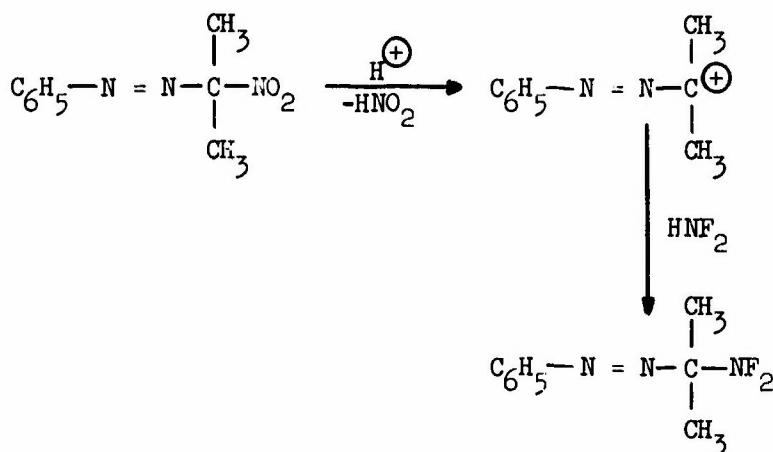
No reaction took place in the absence of a catalyst. An attempt will be made to displace the phenylazo group in this product by a nitration reaction.

Nitroacetaldehyde phenylhydrazone was prepared by diazonium coupling with nitromethane.[*] This compound did not react with neat liquid difluoramine, and when sulfuric acid was added, a black tar was formed from which no product could be isolated.

B.   EXPERIMENTAL

1.   Reaction of Picryl Chloride with Difluoramine

Picryl chloride (5 g) was placed in a 400 ml glass reactor fitted with Fischer-Porter glass and Teflon needle valves, and 18 ml of difluoramine was condensed into the reactor under a nitrogen stream. The reactor was sealed and the contents were allowed to stand at ambient temperature for 73 hours. Unreacted difluoramine was removed. A solid remained which was dissolved in 25 ml of methylene chloride. The infrared spectrum and melting point (80-81°C) of a stripped aliquot were identical with those of the starting material.

To a solution of 2.48 g (0.01 moles) of picryl chloride in 3 ml of refluxing difluoramine, 0.8 g (0.01 moles) of pyridine was added

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[*] E. Bamberger, Chem. Ber., 31, 2629 (1898).

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dropwise over a 45-min period. After 1 hour, 5 ml of methylene chloride was
added and the unreacted difluoramine was removed. Evaporation of the solvent
left a red solid which melted over a broad range (110-160°C) and which did not
contain fluorine.

2.   Reaction of Ethyl Azodicarboxylate with Difluoramine

A mixture of 1.0 g of ethyl azodicarboxylate[*] and 3 ml of
liquid difluoramine was allowed to reflux under nitrogen for 3 hours. Removal
of the difluoramine left 1.0 g of the starting material, with no change in its
infrared spectrum.

3.   Reaction of Ethyl Diazoacetate with Difluoramine

A solution of 1.14 g (0.01 mole) of ethyl diazoacetate[**] in
3 ml of liquid difluoramine was allowed to reflux for 40 min. Methylene
chloride (5 ml) was added and the difluoramine was removed. The infrared
spectrum of the remaining solution was identical with that of ethyl diazoacetate.

A similar experiment with the addition of 1.2 g of potassium
fluoride to the difluoramine solution gave the same results.

In another experiment, 1 ml of concentrated sulfuric acid was
added dropwise over a 30-min period to the difluoramine solution. After 2 hours,
5 ml of methylene chloride was added and the excess difluoramine was vented off.
The reaction mixture was drained on to 10 ml of ice. The methylene chloride
layer was separated and was dried over sodium sulfate. The solvent was removed
at ambient temperature by gradually reducing the pressure to 20 mm. The product
was collected in a -80°C trap while the pressure in the system was lowered from
20 to 0.01 mm. A 14% yield (0.2 g) of ethyl difluoraminoacetate was obtained.
The infrared and NMR spectra of the material were identical with those reported
previously.[***]

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[*] N. Rabjohn (Editor), Organic Synthesis, Collective Volume 4, p. 411, John
Wiley and Sons, Inc., New York, N.Y., 1963.

[**] Ibid, p. 425.

[***] Aerojet-General Report 2730, October 1963, p. 34 (Confidential).

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4.   Reaction of 2-Phenylazo-2-Nitropropane with Difluoramine

        Sulfuric acid (2 ml) was added dropwise to a solution of 2.00 g
(0.3 mmoles) of 2-phenylazo-2-nitropropane* in 3 ml of refluxing difluoramine.
Methylene chloride (10 ml) was added after 3 hours, and the excess difluoramine
was removed. The methylene chloride solution was dried over sodium sulfate.
The solvent was removed at reduced pressure, and the product was vacuum-
transferred into a -80°C receiver at 0.01 mm Hg. The product, which weighed
0.22 g (21% yield), was identified as 2-phenylazo-2-difluoraminopropane.

        Anal. Calc'd for $C_9H_{11}N_3F_2$:   C, 54.3; H, 5.54; N, 21.1; F, 19.1.

                        Found: C, 53.38; H, 5.25; N, 20.27; F, 18.2.

        The F^{19} NMR spectrum contained only a slightly broadened
singlet at -25.3 ϕ. The proton spectrum contained a complex aromatic multiplet
at 7.4 to 8.0 δ, a symmetrical triplet at 1.5 δ, J=1.8 cps, and a small singlet
at 1.2 δ. The latter was apparently due to acetone present at a contaminant.

        An attempted uncatalyzed reaction of 2-phenylazo-2-nitro-
propane and difluoramine gave only recovered starting material.

5.   Reaction of Nitroacetaldehyde Phenylhydrazone with Difluoramine

        Nitroacetaldehyde phenylhydrazone was synthesized from
benzenediazonium ion and nitroethane.** This intermediate (1.8 g) was stirred
with refluxing difluoramine (3 ml) for 30 min, and 8 ml of methylene chloride
was added. At all times a separate solid phase was present. The difluoramine
was vented off and the solid was isolated by filtration, and was washed with
25 ml of methylene chloride. The solid (1.4 g) was identified as starting
material by its infrared spectrum and melting point (140°C).

        In another experiment, 5 ml of sulfuric acid was added dropwise
to a refluxing mixture of 1.4 g of the phenylhydrazone and 3 ml of difluoramine.
The mixture became black. Quenching with ice gave a black emulsion from which
no products could be separated.

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*C. F. Feasley and E. F. Degering, J. Org. Chem., 8, 12 (1943).
**E. Bamberger, Chem. Ber., 31, 2629 (1898).

III. FLUORAMMONIUM PERCHLORATE (V. Grakauskas)

This year's program has included a process study leading to the preparation of several pounds of fluorammonium perchlorate (SAP). The process that was developed is based on the reaction between isopropyl N-fluorocarbamate and anhydrous perchloric acid.[*] With this process, high-purity SAP is obtained in 90-95% yields. The material is presently produced in lots of 70-140 g.

The synthesis of SAP from isopropyl N-fluorocarbamate and 70% aqueous perchloric acid[**] sufficed in the preparation of gram-quantities of the material in the laboratory. Large scale (50-100 g) preparation of SAP based on this procedure appeared to be impractical. The process would require large amounts of starting materials and a relatively elaborate remote-control dry box installation. In addition, the purification of crude material obtained from 70% perchloric acid reaction is quite time-consuming. For these reasons it was decided not to attempt to adopt this procedure for the scale-up operation, but instead to explore other potential routes for the preparation of SAP.

The utilization of anhydrous perchloric acid for the preparation of SAP had been considered at one time, but no experimental work was carried out since it was thought that aqueous perchloric acid would suffice. The unsatisfactory yield, and especially the low purity of SAP obtained in 70% perchloric acid, led to experimentation with the anhydrous acid. It was found that isopropyl N-fluorocarbamate reacts readily with anhydrous perchloric acid at ambient temperature in methylene chloride or chloroform solution to yield SAP in virtually quantitative amounts.[***] Elemental analysis and differential thermal analysis (DTA) showed that the product was of high purity.

The reaction between anhydrous perchloric acid and isopropyl N-fluorocarbamate proceeds as follows:

$$NHFCO_2C_3H_7 + 2HClO_4 \xrightarrow{(CHCl_3)} NH_3F^{\oplus} ClO_4^{\ominus} + CO_2 + C_3H_7ClO_4$$

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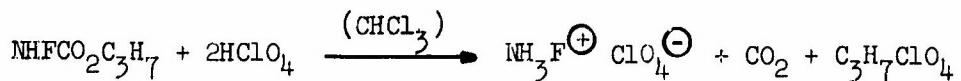
[*] Aerojet-General Report 0235-01-25/26 (Semiannual), September 1966, p. 13 (Confidential).
[**] Aerojet-General Report 2945 (Summary), October 1964, p. 34 (Confidential).
[***] Aerojet-General Report 0235-01-25/26 (Semiannual), September 1966, p. 14 (Confidential).

Isopropyl N-fluorocarbamate in chloroform solution was added to the anhydrous perchloric acid in chloroform solution. The rate of the reaction was followed by carbon dioxide evolution. The reaction was mildly exothermic and could be completed in a matter of minutes at 20 to 30°C.

After the successful laboratory experiments, the preparation of SAP was scaled up to batches ranging in size from 60 to 140 g. This entire large-scale operation was carried out remotely.* The results of scale-up operation are reported in Table 1.

The storage of SAP presented some problems. Earlier work had showed that SAP could be stored for several months at ambient temperature in nickel containers.** Nevertheless, attack on the walls of nickel containers was apparent when larger quantities of SAP were stored at ambient temperatures for 1 to 2 weeks. Pretreating of the nickel containers with HF appeared to alleviate the corrosion problem. Careful removal of chloroform and methylene chloride from SAP during its preparation was found to be very important. Trace amounts of these solvents reduce greatly the stability of the material on prolonged storage.

It was observed that SAP prepared from anhydrous perchloric acid may exist in at least two different crystalline forms.*** When the material was prepared in chloroform solution, it was usually (but not always) obtained in the form of a coarse crystalline solid. This form appears to be metastable and rearranged, with an increase in the bulk density and a decrease in crystal size, after a few days at room temperature. High-bulk-density SAP was obtained directly when the reaction between isopropyl N-fluorocarbamate and anhydrous perchloric acid was carried out in methylene chloride solution instead of in chloroform.

Isopropyl N-fluorocarbamate, required for the preparation of SAP, was obtained by the fluorination of isopropyl carbamate in acetonitrile. The

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*Aerojet-General Report 0235-01-25/26, September 1966, p. 17 (Confidential).
**Aerojet-General Report 0235-01-23, August 1965, p. 15 (Confidential).
***Aerojet-General Report 0235-01-25/26, September 1966, p. 15 (Confidential).

crude isopropyl N-fluorocarbamate was contaminated with isopropyl carbamate and isopropyl N,N-difluorocarbamate. The latter material is volatile and can be readily removed from the mixture, but the separation of isopropyl N-fluorocarbamate from the starting material is difficult. It was found that the mixture can be separated by column chromatography on a silica gel column.[*] The N-fluoro-derivative can be readily eluted with methylene chloride and thus separated from isopropyl carbamate. This purification procedure, in conjunction with fractionation, was employed to obtain pound quantities of isopropyl N-fluoro-carbamate.

IV.   SOME REACTIONS OF 2,2-DINITRO-2-FLUOROETHANOL (V. Grakauskas)

A.   DISCUSSION

During the course of direct fluorination studies, unusual starting materials have on occasion been synthesized and their chemical reactions investigated. Although not directly related to the fluorination work, these reactions appear to be of general interest, and are reported here.

Ethyl 2,2-dinitro-2-fluoroethylcarbamate was obtained when an aqueous mixture of 2,2-dinitro-2-fluoroethanol and ammonium hydroxide was treated with ethyl chloroformate.[**] The major product of this reaction was ethyl 2,2-dinitro-2-fluoroethyl carbonate, indicating that 2,2-dinitro-2-fluoroethanol, unlike 2,2,2-trinitroethanol, reacts relatively slowly with ammonia. On further consideration of the above reaction, it appeared that in aqueous alkaline solution, 2,2-dinitro-2-fluoroethanol may exist in the form of alkoxide anion:

$$FC(NO_2)_2CH_2OH + OH^\ominus \rightleftharpoons FC(NO_2)_2CH_2O^\ominus + H_2O$$
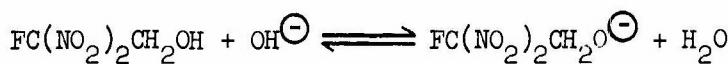
If this were the case, 2,2-dinitro-2-fluoroethanol would be expected to react with alkylating agents in the alkaline medium to give the corresponding ethers:
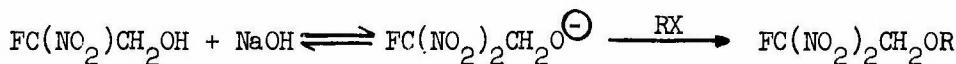
$$FC(NO_2)CH_2OH + NaOH \rightleftharpoons FC(NO_2)_2CH_2O^\ominus \xrightarrow{RX} FC(NO_2)_2CH_2OR$$

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[*] Aerojet-General Report 0235-01-25/26, September 1966, p. 15 (Confidential).

[**] Aerojet-General Report 0235-01-18, January 1954, p. 20ff (Confidential).

This was found to be the case. 2,2-Dinitro-2-fluoroethyl methyl ether was obtained when 2,2-dinitro-2-fluoroethanol was reacted with methyl sulfate in the presence of sodium hydroxide:

$$FC(NO_2)_2CH_2OH + (CH_3)_2SO_4 + NaOH \xrightarrow{(H_2O)} FC(NO_2)_2CH_2OCH_3$$
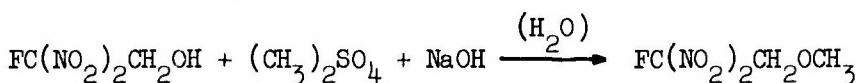
The compound was characterized on the basis of its elemental analysis, its infrared spectrum (Figure 2), and its proton and fluorine NMR spectra.[*] Under similar reaction conditions, 2,2-dinitro-2-fluoroethanol reacted with allyl bromide to give allyl 2,2-dinitro-2-fluoroethyl ether:

$$FC(NO_2)_2CH_2OH + NaOH + BrCH_2CH=CH_2 \xrightarrow{(H_2O)} FC(NO_2)_2CH_2OCH_2CH=CH_2 + NaBr$$
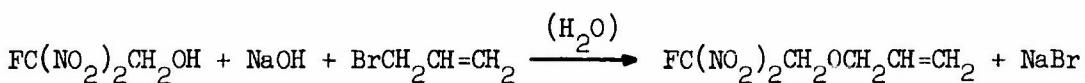
The compound was identified on the basis of its elemental analyses, and its infrared (Figure 3) and NMR spectra.

Differential thermal analyses of methyl and allyl 2,2-dinitro-2-fluoroethyl ethers showed endotherms of about 180 and 205°C, respectively.

These reactions of 2,2-dinitro-2-fluoroethanol suggest that, in general, the alcohol should undergo alkylation with a variety of other alkylating agents to give the corresponding mixed ethers, which may be useful as energetic plasticizers or polymerizable monomers. The unsaturated ethers, such as the allyl 2,2-dinitro-2-fluoroethyl ether, would be expected to add N_2F_4 or HNF_2 to give "mixed" nitro-difluoramino ethers.

An attempted preparation of 2,2-dinitro-2-fluoroethylamine in a Mannich reaction[**] led to an explosion. It appeared that the compound could be obtained in the hydrolysis of 2,2-dinitro-2-fluoroethyl carbamates:

$$FC(NO_2)_2CH_2NHCO_2R \xrightarrow{(acid)} FC(NO_2)_2CH_2NH_3^{\oplus} + CO_2 + ROH$$
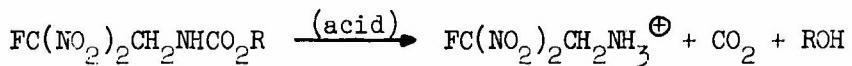
Isopropyl 2,2-dinitro-2-fluoroethyl carbamate underwent decarboxylation on dissolution in concentrated sulfuric acid at room temperature, and a white

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[*] Previously prepared by another method, Naval Ordnance Laboratory Report NOLTR 65-67, 9 August 1965, p. 11 (Confidential).

[**] Aerojet-General Report 2945 (Summary), October 1964, p. 24 (Confidential).

IV Some Reactions of 2,2-Dinitro-2-Fluoroethanol, A (cont.)   Report No. 3299

crystalline solid was obtained when the reaction mixture was diluted with diethyl ether. However, the material decomposed spontaneously on attempted isolation. The compound was characterized as 2,2-dinitro-2-fluoroethylammonium salt in sulfuric acid solution by its fluorine and proton NMR spectra.

Finally, 2,2-dinitro-2-fluoroethanol was shown to react in a Mannich type reaction with methoxyamine to give 2,2-dinitro-2-fluoroethyl methoxyamine:

$$FC(NO_2)_2CH_2OH + NH_2OCH_3 \xrightarrow{(H_2O)} FC(NO_2)_2CH_2NHOCH_3$$
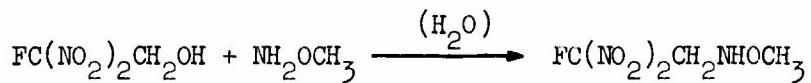
The pure compound was not isolated in this case, but its structure was established on the basis of its proton and fluorine NMR spectra.

B.   EXPERIMENTAL

1.   2,2-Dinitro-2-Fluoroethyl Methyl Ether

Dimethyl sulfate (5.1 g, 0.04 mole) was added at 25°C to a stirred solution of 6.2 g (0.04 mole) of 2,2-dinitro-2-fluoroethanol in 40 ml of water. Then a solution of 2.0 g (0.05 mole) of sodium hydroxide in 15 ml of water was added drop by drop. The reaction was mildly exothermic, and the reaction mixture warmed by itself to 29-33°C. Ten minutes later when the addition of the sodium hydroxide solution was complete, the reaction mixture was stirred for an additional 45 min and then extracted with 30 ml of methylene chloride. The methylene chloride solution was distilled to give 5.5 g of a colorless liquid, b.p. 74-76°C/40 mm. The infrared spectrum of the product showed a small amount of dimethyl sulfate as a contaminant. The material was washed with 5% aqueous sodium hydroxide to remove the contaminant, and the ether was redistilled, b.p. 27°C/0.1 mm, n_D^{25} 1.4045, weight 4.8 g (71% yield).

Anal. Calc'd for $C_3H_5N_2FO_5$:   C, 21.4; H, 3.0; N, 16.7; F, 11.3.

Found: C, 21.1; H, 2.7; N, 15.7; F, 10.6.

The infrared spectrum of the material (Figure 2) is consistent with the structure.

IV Some Reactions of 2,2-Dinitro-2-Fluoroethanol, B (cont.)   Report No. 3299

The F^{19} NMR spectrum exhibited one signal as a broadened band at ϕ = 110.9 (CFCl$_3$ used as internal reference). This chemical shift value indicates fluorine of FC(NO$_2$)$_2$-moiety.

The proton NMR spectrum consisted of a doublet (J_{HF} = 18 cps) centered at δ = 4.60 representing -CH$_2$O- (relative area 151), and a singlet at δ = 3.6 (relative area 223) representing OCH$_3$.

2.   Allyl 2,2-Dinitro-2-Fluoroethyl Ether

A solution of 1.6 g (0.04 mole) of sodium hydroxide in 20 ml of water was added to a stirred suspension of 4.62 g (0.03 mole) of 2,2-dinitro-2-fluoroethanol and 4.85 g (0.04 mole) of allyl bromide in 30 ml of water at 25°C. The reaction mixture was stirred for a period of 2 hours at 25-28°C and then extracted with 30 ml of methylene chloride. The methylene chloride solution was distilled to give 2.5 g of a colorless liquid, b.p. 31-33°C/0.2 mm. The product was found to be contaminated with a small amount of 2,2-dinitro-2-fluoroethanol; it was washed with two 10 ml portions of water, phases separated, and the ether was submitted for analyses.

Anal. Calc'd for C$_5$H$_7$N$_2$FO$_5$:   C, 30.9; H, 3.6; N, 14.4; F, 9.8.

Found: C, 30.0; H, 3.4; N, 13.8; F, 9.9.

The infrared spectrum of the material (Figure 3) was consistent with the structure.

NMR spectra of 2,2-dinitro-2-fluoroethyl methyl ether were recorded using pure compound. The F^{19} spectrum displays a triplet ($J_{HF} \simeq$ 15 cps) at ϕ = 111.0 (Freon-11 used as internal reference). This chemical shift region is indicative of fluorine in the fluorodinitromethyl moiety.

The proton NMR spectrum (TMS used as an internal reference) consisted of the following signals:

a.   Between δ = 5.56 and 6.20, the characteristic 12-line pattern (doublet of doublets of triplets; J_{cis} = 9 cps, J_{trans} = 17.5 cps, J_{allyl} = 5.5 cps) of the internal olefin proton at a terminal vinyl group (area 67).

IV Some Reactions of 2,2-Dinitro-2-Fluoroethanol, B (cont.)   Report No. 3299

   b.   Between $\delta = 5.06$ and 5.51, the superposition of multiplets for the external olefin protons of the vinyl group (area 150).

   c.   Centered at $\delta = 4.58$, the doublet ($J_{HF} = 18$ cps) of the CH_2 in the fluorodinitroethyl moiety (area 144).

   d.   Centered at $\delta = 4.15$, the doublet ($J = 5.5$ cps) of the allylic CH_2 (area 150).

   The proton and F^{19} NMR spectral data are consistent with each other and with the structure, $FC(NO_2)_2CH_2OCH_2CH=CH_2$.

   3.   2,2-Dinitro-2-Fluoroethylammonium Bisulfate

   Isopropyl 2,2-dinitro-2-fluoroethylcarbamate* (0.2 g) was added with stirring to 1.0 ml of concentrated sulfuric acid. Carbon dioxide was evolved. After 15 min, the reaction mixture was added to 50 ml of diethyl ether and the solution was kept at $-15^{\circ}C$ for 18 hours, resulting in precipitation of a white crystalline solid. The material was filtered and washed with four 10-ml portions of diethyl ether. The solid fumed off when it was removed from the sintered glass funnel.

   The above reaction between sulfuric acid and the carbamate was repeated, and the resulting reaction mixture was submitted for NMR analysis.

   The fluorine NMR spectrum showed one signal: a triplet ($J \cong 10$ cps) centered at 26.2 ppm upfield from external trifluoroacetic acid standard. This corresponds to $\phi = 101$ ppm (relative to $CFCl_3$ internal standard). This signal is assigned to $\underline{F}C(NO_2)_2-$ fluorine.

   The proton NMR spectrum exhibits a strong H_2SO_4 signal, and also a broad symmetrical band at $\delta = 6.6$ (relative area = 153) along with a symmetrical six-line pattern centered at $\delta = 4.0$ (relative area = 102). These

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*The compound, together with larger quantities of 2,2-dinitro-2-fluoroethyl isopropyl carbonate, was obtained from 2,2-dinitro-2-fluoroethanol ammonium hydroxide and isopropyl chloroformate following the procedure used for the preparation of ethyl derivative (see Aerojet General Report 0235-01-18, January 1964, p. 29). The compound is a white solid, m.p. $47-48^{\circ}C$. Anal. Calc'd for $C_6H_{10}N_3FO_6$: C, 30.1; H, 4.2; N, 17.6; F, 7.9. Found: C, 29.8; H, 3.9; N, 16.1; F, 7.9.

IV Some Reactions of 2,2-Dinitro-2-Fluoroethanol, B (cont.)   Report No. 3299

signals are attributed to $-C-NH_3$ and $-CH_2N-$ protons, respectively. The $NH_3^{\oplus}$ signal is apparently broadened by slow exchange; the $-CH_2-$ signal is apparently a doublet (J_{HF} = 11 cps) of quartets (J_{NH-H} = 6 cps).

The fluorine and proton NMR spectra are consistent with each other and the relative area ratio of $NH_3^{\oplus}$ to CH_2 points to the desired structure, $FC(NO_2)_2CH_2NH_3^{\oplus}$.

4.   2,2-Dinitro-2-Fluoroethylmethoxyamine

Sodium bicarbonate (0.85 g, 0.01 mole) at 25°C was added to a solution of 0.84 g (0.01 mole) of methoxyamine hydrochloride and 1.54 g (0.01 mole) of 2,2-dinitro-2-fluoroethanol in 15 ml of water. The reaction mixture was stirred vigorously for a period of 3 hours. At the end of the run, approximately 1 ml of water-insoluble liquid was present in the reaction flask. The product was extracted with two 7-ml portions of methylene chloride and the solution was submitted for NMR analysis. The F^{19} NMR spectrum showed a broadened band at ϕ = 109.5, which was attributed to fluorine of $FC(NO_2)_2CH_2-$. The proton NMR spectrum showed a broad band at δ = 6.1, which was attributed to the $-CH_2NH-$ proton. The band disappeared on addition of D_2O (relative area ~ 15). A doublet (J_{HF} = 16 cps) of doublets centered at δ = 4.21 (relative area = 47) was attributed to $-CH_2NH-$ (changes to doublet on addition of D_2O). A sharp singlet at δ = 3.45 (relative area = 80) was attributed to $-OCH_3$. The material was contaminated with 2,2-dinitro-2-fluoroethanol and dinitrofluoromethane.

V.   SUMMARY

A.   REACTIONS OF DIFLUORAMINE

Reactions of diazonium salts with N-fluorocarbamates in the presence of mild bases gave azides and alkyl fluoroformate.

Reactions of diazonium salts with difluoramine gave aromatic azides with fluorine introduced into the ortho or para position. When all ortho and para positions were blocked by substituents, aromatic azides were formed, and fluorine was apparently consumed by reaction with difluoramine. Reduction of diazonium groups also occurred, apparently favored by electron-withdrawing substituents.

V Summary, A (cont.)   Report No. 3299

The reaction 2,5,8-triketononane with difluoramine and fuming sulfuric acid gave 2-methyl-2,5-bis(difluoramino)-5-[γ,γ-bis(difluoramino)butyl] tetrahydrofuran.

No reaction took place between picryl chloride and neat liquid difluoramine in 73 hours. The addition of pyridine gave no fluorine-containing products.

The reaction ethyl diazoacetate with difluoramine and sulfuric acid gave ethyl difluoraminoacetate. Ethyl azodicarboxylate did not react with difluoramine, and nitroacetaldehyde phenylhydrazone gave only tars. 2-Phenylazo-2-nitropropane was converted to 2-phenylazo-2-difluoraminopropane.

B.   FLUOROAMMONIUM PERCHLORATE

High-purity fluoroammonium perchlorate (SAP) was obtained in high yield from isopropyl N-fluorocarbamate and anhydrous perchloric acid. This reaction was developed into a process capable of producing hundred-gram quantities of the material per run. The salt is now readily available in pound quantities, and experimental samples were supplied to other organizations for thermochemical and formulation studies.

C.   REACTIONS OF 2,2-DINITRO-2-FLUOROETHANOL

Alkylation and Mannich condensation reactions of 2,2-dinitro-2-fluoroethanol were briefly investigated. 2,2-Dinitro-2-fluoroethyl methyl and 2,2-dinitro-2-fluoroethyl allyl ethers were obtained as O-alkylation products on treatment of alkaline solutions of 2,2-dinitro-2-fluoroethanol with dimethyl sulfate and allyl bromide, respectively.

VI.   CONCLUSIONS AND RECOMMENDATIONS

A.   REACTIONS OF DIFLUORAMINE

1-Aryl-3-fluorotriazenes and 1-aryl-3,3-difluorotriazenes are unstable. The former decompose by a 1,2-fluorine shift, and the latter by fluoride ionization and rearrangement, or by homolytic cleavage.

The reaction of picryl chloride and similar compounds with difluoramine does not appear to be a feasible method of preparing aromatic difluoramines.

VI Conclusions and Recommendations, A (cont.)　　　　　Report No. 3299

Alkyldifluoramines can be prepared from diazoalkanes and difluoramine.

The nitro group of 2-phenylazo-2-nitropropane is more reactive toward HNF_2-H_2SO_4 than is the azo group. It appears possible that compounds with nitro and difluoramino groups on the same carbon atom can be prepared by the nitration of the product of the above reaction and its analogs.

B.　　FLUOROAMMONIUM PERCHLORATE

The process used for the preparation of fluoroammonium perchlorate is now well understood and is ready for further scaleup if larger quantities of the salt are required. Improvements in the preparation and purification techniques for the starting material in the process, isopropyl N-fluorocarbamate, would be highly desirable for a more economical large-scale operation.

C.　　REACTIONS OF 2,2-DINITRO-2-FLUOROETHANOL

Some of the dinitrofluoromethyl derivatives obtained in the alkylation and Mannich reactions of 2,2-dinitro-2-fluoroethanol might serve as useful starting materials for the preparation of mixed nitro-difluoramino compounds.

TABLE 1

LARGE-SCALE PREPARATION OF SAP

Experiment No.	Anhydrous HClO$_4$, g	NHFCO$_2$C$_3$H$_7$ g	Solvent[1]	Yield of SAP g	Yield of SAP %	Elemental Analysis[2], Found (%): C	H	N	F
21	94	56.6	C	63	100	0.1	2.6	10.1	13.6
27	101.5	60.8	C	57.7		0.2	2.5	9.8	13.9
32	98	58.5	C	61	93	0.1	2.2	10.0	13.9
34	202	121	C	135	99	0.5[3]	2.7	9.0	13.5
40	81.5	48.9	M	48	86	0.1	2.4	9.5	14.2
42	92	55	C	51		0.1	2.4	9.7	13.8
44	79	46.8	C	40	77	0.1	2.4	9.8	13.7
64	101	60.6	C	58	85	0.1	2.4	9.9	13.9
69	117	65	C	64	90	0.1	2.4	10.2	14.2
73	110	60.5	C	63	93	0.0	2.4	10.0	13.9
75	107	59	C	60	92	0.1	2.4	9.9	13.8

[1] C = chloroform; M = methylene chloride.
[2] Calculated for NH$_3$FClO$_4$: C, 0.0; H, 2.2; N, 10.2; F, 14.0.
[3] Contamination with solvent responsible for high carbon analysis.
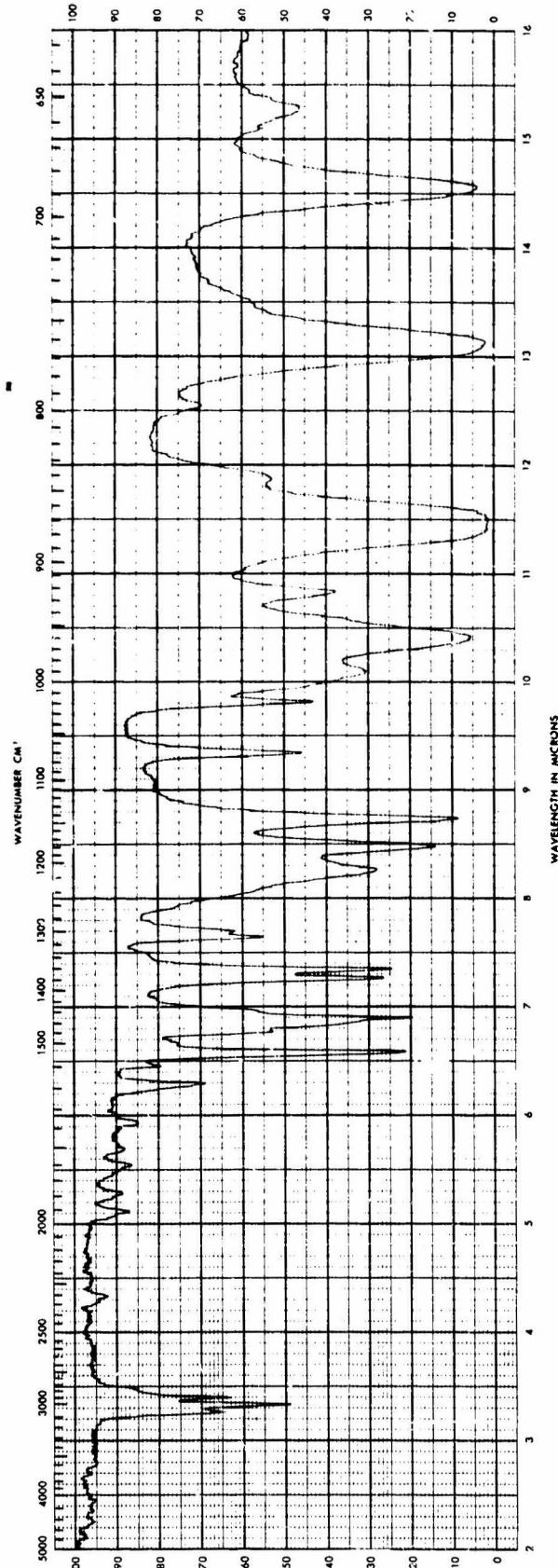
Infrared Spectrum of 2-Phenylazo-2-difluoraminopropane

Infrared Spectrum of 2,2-Dinitro-2-fluoroethyl Methyl Ether

Infrared Spectrum of 2,2-Dinitro-2-fluoroethyl Allyl Ether