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REPORT NO. 0235-01-25/26 (SEMIANNUAL)
PERIOD COVERED: 1 JANUARY - 30 JUNE 1966

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

A REPORT TO

OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

CONTRACT Nonr 2655(00)
ARPA ORDER 170, AMENDMENT 8
PROGRAM CODE 5H10

SEPTEMBER 1966

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

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(0235)

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September 1966

Report No. 0235-01-25/26
(Semiannual)

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

By

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Analytical Support: K. Inouye

A Report to
OFFICE OF NAVAL RESEARCH
and
ADVANCED RESEARCH PROJECTS AGENCY

Contract Nonr 2655(00)
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Program Code 5H10

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

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Report No. 0235-01-25/26

ABSTRACT

Reactions of aryldiazonium salts with difluoramine were studied with the objective of synthesizing aryldifluoramines. The products of these reactions, however, were fluoroaryl azides or aromatic hydrocarbons, depending on the nature of the benzenediazonium salts.

Phenyl azide and isopropyl fluoroformate were obtained in the reaction between isopropyl N-fluorocarbamate and benzenediazonium fluoborate. Analogous reactions were encountered with o-, m-, and p-nitrobenzenediazonium fluoborates.

Fluorammonium perchlorate (SAP) was obtained quantitatively in the reaction between isopropyl N-fluorocarbamate and anhydrous perchloric acid. A process based on this reaction was developed, and SAP is now being produced in lots of 70 to 140 g.

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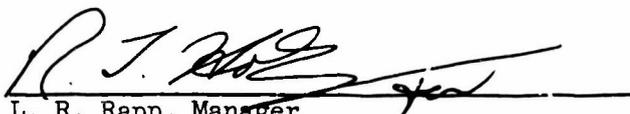
CONTRACT FULFILLMENT STATEMENT

This semiannual technical report is submitted in partial fulfillment of the contract and covers the period from 1 January through 30 June 1966.

AEROJET-GENERAL CORPORATION



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I. INTRODUCTION

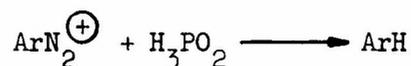
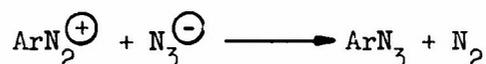
The objective of this program is to develop new methods of preparing high-energy materials of interest for military applications.

II. REACTIONS OF DIAZONIUM SALTS WITH DIFLUORAMINE (K. Baum)

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.

A. DISCUSSION

Most reactions of diazonium salts fall within the classes of (1) coupling, with or without loss of nitrogen, and (2) reduction, typified by reactions with azide, aniline, and hypophosphorous acid, as follows:**



By these routes difluoramine could be expected to yield aromatic difluoramines, difluorotriazenes, or aromatic hydrocarbons.

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

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

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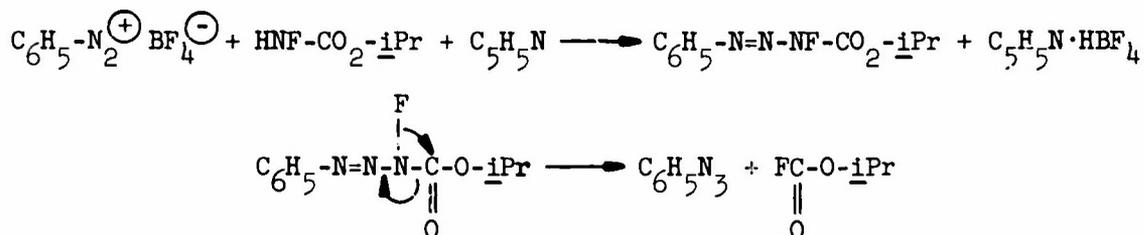
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II Reactions of Diazonium Salts with
Difluoramine, A (cont.)

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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:



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-nitrobenzenediazonium fluoborate, m-nitrobenzenediazonium fluoborate, and p-nitrobenzenediazonium 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.

* K. O. Christi and A. E. Pavlath, J. Org. Chem., 30, 1639 (1965).

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

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II Reactions of Diazonium Salts with
Difluoramine, A (cont.)

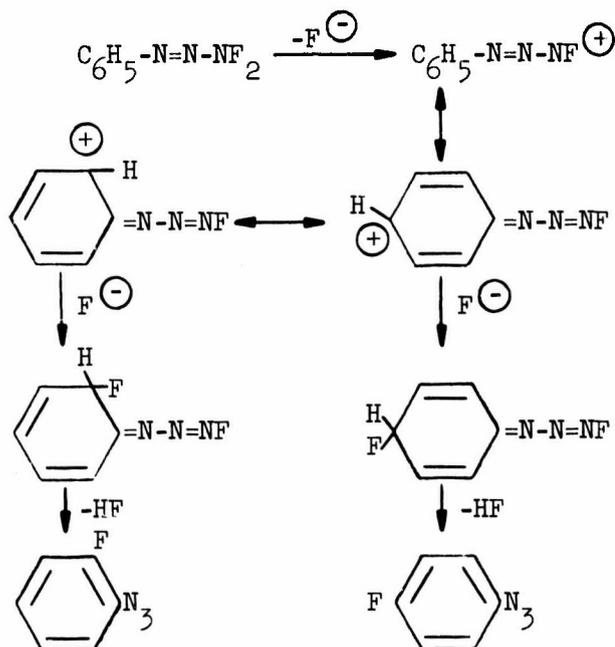
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The infrared spectrum of the product soluble in methylene chloride showed strong azide absorption at 4.7μ . The F^{19} nuclear-magnetic-resonance (NMR) spectrum contained peaks at 118.1 and 127.5 ϕ , which were shown to be due to p-fluorophenyl azide, 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.

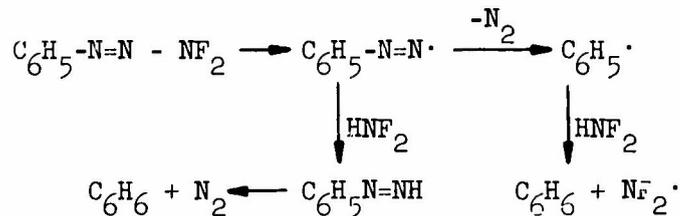
Although potassium fluoride was effective in promoting this reaction, sodium fluoride gave no reaction, probably because of the much greater solubility of sodium fluoborate. On the other hand, the addition of a trace of cesium fluoride to the difluoramine solution of the diazonium salt resulted in a 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.

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:

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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:



Reactions of other diazonium salts with difluoramine were also studied. *p*-Nitrobenzenediazonium fluoborate gave mainly nitrobenzene, but an azide was also detected; identification is incomplete. *p*-Methoxybenzenediazonium fluoborate gave an azide, but no anisole was detected.

* Smith, op. cit.

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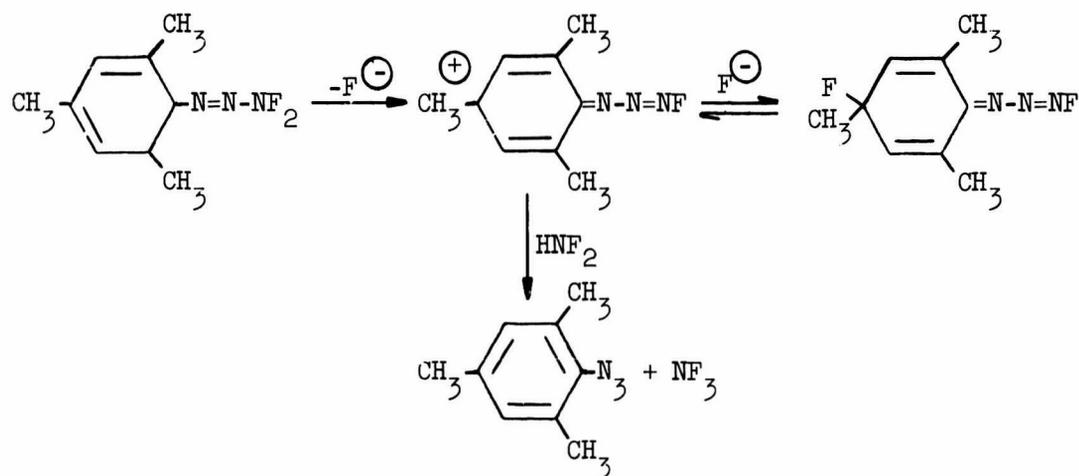
II Reactions of Diazonium Salts with
Difluoramine, A (cont.)

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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 fluoride - 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:



* L. Blangey, Helv. Chim. Acta, 8, 782 (1925).

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B. EXPERIMENTAL

1. Difluoramine Generation

The previously described* procedure for generating difluoramine from aqueous difluorourea solution was modified in a way that was found more convenient for small quantities of difluoramine.

Difluorourea solution (100 ml) was added, dropwise with stirring, to 300 ml of concentrated sulfuric acid in a 500-ml three-necked flask. The generator flask was fitted with a nitrogen inlet, a thermometer, and a trap filled with Drierite that was connected in turn to a reaction flask fitted with a -80°C condenser and a thermometer. A slow nitrogen flow was maintained during the reaction. The rate of addition of difluorourea solution to sulfuric acid was such as to maintain a temperature of 80 to 90°C . No external heating was required.

2. Reactions of Isopropyl N-Fluorocarbamate

a. With Benzenediazonium Fluoborate

A stirred mixture of 1.21 g (0.01 mole) of isopropyl N-fluorocarbamate, 2.0 g (0.0104 mole) of benzenediazonium fluoborate, and 10 ml of methylene chloride was flushed with a slow stream of nitrogen and was cooled to -10°C . Potassium fluoride (2.0 g, 0.034 mole) was added in several portions, and the reaction mixture was kept at 0 to 5°C for 1 hour. The solution was filtered. Its infrared spectrum indicated only phenyl azide and isopropyl fluoroformate. Phenyl azide was characterized further by gas chromatography (10-ft column of 10% dioctyl phthalate on Teflon, 110°C , 60 ml of helium per minute), by comparing its retention time and the infrared spectrum of a trapped sample with an authentic sample of phenyl azide. Isopropyl fluoroformate was not separated from the solvent with this column.

Isopropyl fluoroformate was isolated in another run conducted in a manner similar to that described above, but with the following starting materials: 3.63 g (0.03 mole) of isopropyl N-fluorocarbamate, 5.73 g (0.03 mole) of benzenediazonium fluoborate, 2.37 g (0.03 mole) of pyridine (instead of

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

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II Reactions of Diazonium Salts with
Difluoramine, B (cont.)

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potassium fluoride), and 30 ml of methylene chloride. The methylene chloride solution of the product was concentrated with the aid of a Holzmman column. Vacuum distillation gave 4.5 g of liquid, b.p. 24°C/400 mm Hg, and 0.5 g of b.p. 23°C/200 mm Hg. The residue contained mainly phenyl azide. The 0.5-g fraction was chromatographed on a 10-ft by 1/4-in. column of 3% Carbowax 4000 on Teflon at 60°C, 45 ml He/min. Two peaks were resolved, the second of which was shown (by infrared and NMR spectra of a trapped sample) to be a mixture of isopropanol and methylene chloride. The material responsible for the first peak was identified as isopropyl fluoroformate.

Anal. Calc'd for $C_4H_7O_2F$: C, 45.28; H, 6.60.
Found: C, 45.39; H, 6.85.

The infrared spectrum showed carbonyl absorption at 5.5 μ . The F^{19} spectrum consisted of a sextet at +16.4 ϕ , which is in the region reported for fluoroformates.*

b. With Nitrobenzenediazonium Fluoborates

A three-necked, 25-ml flask (fitted with a thermometer, a nitrogen inlet, a magnetic stirrer, and a bent closed-end tube containing 1.2 g (0.02 mole) of potassium fluoride) was loaded with 10 ml of methylene chloride, 2.37 g (0.01 mole) of *o*-nitrobenzenediazonium fluoborate, and 1.21 g (0.01 mole) of isopropyl N-fluorocarbamate. The flask was cooled to 0°C and the potassium fluoride was added slowly, with stirring. After 5 min the flask was allowed to warm to room temperature, and stirring was continued for 45 min. The solution was filtered and the precipitate was washed with 25 ml of methylene chloride. Solvent was removed from the combined methylene chloride solutions with the aid of a rotary evaporator and aspirator. The residue, an oil, was crystallized from pentane to give 1.61 g (98% yield) of *o*-nitrophenyl azide, m.p. 51 to 52°C (reported value,** 53°C).

Starting with *m*-nitrobenzenediazonium fluoborate, the identical procedure gave 1.40 g (85% yield) of *m*-nitrophenyl azide, m.p. 51 to 53°C (reported value,*** 55°C).

* Christi and Pavlath, op. cit.
** Zincke and Schwarz, op. cit.
*** Noelting, Grandmougin, and Michel, op. cit.

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II Reactions of Diazonium Salts with
Difluoramine, B (cont.)

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Similarly, p-nitrobenzenediazonium fluoborate gave 1.3 g (79% yield) of p-nitrophenyl azide, m.p. 68°C (reported value,* 70°C).

The three azides gave satisfactory elemental analyses.

The above reactions were also conducted with pyridine rather than potassium fluoride as the base. Thus, 2.37 g (0.03 mole) of pyridine was added at 0 to 5°C, dropwise with stirring, to a stirred mixture of 3.63 g (0.03 mole) of isopropyl N-fluorocarbamate, 5.73 g (0.0242 mole) of p-nitrobenzenediazonium fluoborate, and 30 ml of methylene chloride. The mixture was kept at 0 to 5°C, with stirring, for 30 min. A precipitate, identified as pyridine fluoborate by its infrared spectrum, was filtered off and washed with methylene chloride. Solvent was removed from the combined solutions to yield 4.6 g of crude p-nitrophenyl azide, m.p. 55 to 60°C. Recrystallization from methylene chloride and pentane gave 2.5 g (63% yield) of product, m.p. 71.5 to 72°C.

Starting with o-nitrobenzenediazonium fluoborate, the same procedure gave 4.8 g of crude product, m.p. 25 to 40°C. Recrystallization as above gave 2.2 g (55% yield) of o-nitrophenyl azide, m.p. 52 to 53°C.

3. Fluorophenyl Azides

Sodium nitrite (0.43 g, 0.0062 mole) was added dropwise to a stirred suspension of 1.0 g (0.0062 mole) of p-fluorophenylhydrazine hydrochloride in 5 ml of water while the reaction temperature was held at 0 to 5°C. The mixture was kept at this temperature for 15 min, and the product was extracted with 3 ml of carbon tetrachloride. The solution was dried over sodium sulfate and was filtered. The F¹⁹ NMR spectrum showed a quintet at 118.1 ϕ .

The same procedure was used to prepare solutions of o-fluorophenyl azide and m-fluorophenyl azide in carbon tetrachloride, employing the corresponding fluorophenylhydrazine hydrochlorides as starting materials. The F¹⁹ signal of o-fluorophenyl azide was an almost symmetrical multiplet at 127.5 ϕ . That of m-fluorophenyl azide exhibited a general quartet profile with additional splitting of the inner members; its position was 112.0 ϕ .

* Rupe and Majewski, op. cit.

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II Reactions of Diazonium Salts with
Difluoramine, B (cont.)

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The spectra of each of these azides also indicated a small amount of fluorobenzene (114 ϕ).

4. Reaction of Benzenediazonium Fluoborate with Difluoramine

To a solution of 5.0 g (0.026 mole) of benzenediazonium fluoborate in approximately 27 g of difluoramine, 2.05 g (0.026 mole) of pyridine was added dropwise, with stirring. After 4.5 hours, the excess difluoramine was vented, and the residue was extracted with 60 ml of methylene chloride. The solvent was removed with a rotary evaporator, and the product was vacuum-transferred to a -80°C receiver at 0.1 mm Hg to yield 0.3 g of liquid. The F^{19} NMR spectrum consisted of a 1:1:1 triplet at -32.5ϕ ($J \approx 46$ cps), a broadened singlet at -26.2ϕ , a "quintet" at $+119 \phi$, and a multiplet at $+127 \phi$. The relative areas of the four peaks were 108:88:385:215, respectively; the latter two signals were identical in position and profile to those of *p*-fluorophenyl azide and *o*-fluorophenyl azide, respectively. Repetition of this reaction under virtually identical conditions failed to give any downfield F^{19} signals.

Pyridine (0.82 g, 0.0104 mole) was added dropwise, with stirring, to a mixture of 2.0 g (0.0104 mole) of benzenediazonium fluoborate and approximately 4.5 g of difluoramine at -40°C . The reaction temperature was allowed to rise to -10°C over a 1-hour period and 10 ml of methylene chloride was then added. Excess difluoramine was vented off, and the remaining solution was filtered. The filtrate was kept at ambient temperature while the solvent was removed by distillation into a -80°C receiver as the pressure was gradually reduced to 100 mm Hg. The pressure was then lowered to 10 μ Hg to yield 0.1 g of distillate. The F^{19} NMR spectrum showed *p*-fluorophenyl azide ($\phi = 118$ ppm) and *o*-fluorophenyl azide ($\phi = 127$ ppm) in a ratio of 62:102. There were no downfield signals.

Potassium fluoride (2.5 g, 0.042 mole) was placed in a bent tube connected to a three-necked flask containing 2.0 g (0.0104 mole) of benzenediazonium fluoborate. Difluoramine (approximately 4.5 g) was generated and was refluxed over the fluoborate, and the potassium fluoride was added in small increments, with magnetic stirring. Methylene chloride (5 ml) was added after 30 min and the difluoramine was vented. The temperature during the reaction period was -5 to 0°C .

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II Reactions of Diazonium Salts with
Difluoramine, B (cont.)

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The solution was filtered and the precipitate was washed with methylene chloride. Solvent was removed from the combined solutions, and vacuum transfer of the residue yielded 0.05 g of product. The F^{19} spectrum showed o- and p-fluorophenyl azides, and barely detectable signals at approximately -32ϕ and -27ϕ .

A mixture of 2.0 g (0.0104 mole) of benzenediazonium fluoborate and 2.0 g (0.034 mole) of potassium fluoride was placed in a three-necked flask and cooled to -80°C while 4.5 g of difluoramine was introduced. The mixture was allowed to reflux for 2 hours and was worked up as described above. The F^{19} NMR spectrum of the product (0.2 g) showed p-fluorophenyl azide and o-fluorophenyl azide in a ratio of 240:190. A weak 1:1:1 triplet was noted at -32ϕ and a broad signal at -25ϕ . Four similar experiments gave no trace of downfield signals. In one such case the NMR spectrum was run at 0°C with a sample obtained by adding 5 ml of carbon tetrachloride to the refluxing difluoramine mixture, venting difluoramine while keeping the solution at 0°C .

Sodium fluoride (1.4 g, 0.033 mole) was added to a refluxing mixture of 2 g (0.0104 mole) of benzenediazonium fluoborate and 4.5 g of difluoramine. After 1 hour, the difluoramine was removed, giving a quantitative recovery of sodium fluoride and benzenediazonium fluoborate.

The reaction was attempted with cesium fluoride instead of sodium fluoride. A detonation occurred when the first trace of cesium fluoride was added. The reaction was repeated with the difluoramine mixture diluted with 10 ml of methylene chloride. A fume-off occurred when the cesium fluoride was added.

A sodium carboxylate type of ion-exchange resin (1 g, Bio-Rex 70) was added to a refluxing mixture of 2 g of benzenediazonium fluoborate and 4.5 g of difluoramine. After 2 hours, 5 ml of methylene chloride was added and the difluoramine was removed. The F^{19} NMR spectrum of the methylene chloride showed essentially no fluorine.

5. Reaction of 2,4,6-Trimethylbenzenediazonium Fluoborate with Difluoramine

To a solution of 2.34 g (0.01 mole) of 2,4,6-trimethylbenzenediazonium fluoborate in 3 ml of refluxing difluoramine, 2.0 g (0.034 mole) of potassium fluoride was introduced by means of an addition tube. The mixture was

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II Reactions of Diazonium Salts with
Difluoramine, B (cont.)

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stirred under reflux for 1.5 hours, and 5 ml of methylene chloride was added. Unreacted difluoramine was vented and the solution was filtered. The precipitate was washed with 50 ml of methylene chloride, and the combined solutions were stripped of solvent in a rotary evaporator. The residue consisted of 1.4 g of oil, the infrared spectrum of which indicated that it was mainly 2,4,6-trimethylphenyl azide containing some mesitylene.* Attempted vacuum distillation of the material resulted in decomposition.

A sample of 2,4,6-trimethylphenyl azide for comparison was prepared by adding a solution of 0.28 g (0.0043 mole) of sodium azide in 5 ml of water to a solution of 1.0 g (0.0043 mole) of 2,4,6-trimethylbenzenediazonium fluoborate in 20 ml of water at 5°C. An oil separated; after 15 min it was extracted with 10 ml of methylene chloride. The solution was dried over sodium sulfate and the solvent was removed under vacuum.

Anal. Calc'd for $C_9H_{11}N_3$: C, 67.1; H, 6.83; N, 26.1.

Found: C, 67.27; H, 6.74; N, 25.41.

The infrared spectrum contained peaks at 3.40 (w), 4.72 (s), 6.2 (w), 6.8 (m), 7.6 (m), 7.8 (m), 9.1 (w), and 11.7 microns (m).

6. Diazotization and Difluoramination of Picramide

Picramide was diazotized in concentrated sulfuric acid using a procedure reported by Blangey.** Sodium nitrite (0.72 g, 0.011 mole) was added slowly, with stirring in a nitrogen atmosphere, to 8 ml of sulfuric acid at 0°C. The solution was heated to 70°C and was then cooled to 0°C. Picramide (2.3 g, 0.01 mole) was added, with stirring, and the mixture was kept at 0°C for 2 hours and then at room temperature for 20 hours.

Difluoramine (4.5 g) was generated from difluorocurea and was allowed to reflux over the above solution for 3 hours. The reaction mixture was drained onto 100 ml of ice, and a solid that precipitated was filtered off and was dissolved in 50 ml of methylene chloride. The methylene chloride solution was dried over sodium sulfate, and the solvent was removed at aspirator pressure to

* No. 4539 in Sadtler Standard Spectra, Philadelphia, Sadtler Research Laboratories, 1962.

** Op. cit.

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Difluorammine, B (cont.)

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give 1.9 g (0.0089 mole, 89% yield) of 1,3,5-trinitrobenzene, m.p. 83 to 87°C. The infrared spectrum of the material was practically identical to that of an authentic sample.

Anal. Calc'd for $C_6H_3N_3O_6$: C, 33.8; H, 1.4; N, 19.7.
Found: C, 33.15; H, 1.40; N, 19.27.

7. Diazotization and Difluoramination of 2,6-Dinitroaniline

The diazotization* of 2,6-dinitroaniline was conducted by adding 0.76 g (0.011 mole) of sodium nitrite to 10 ml of sulfuric acid at 2°C, with stirring and a nitrogen sweep. The solution was heated to 70°C and was cooled again to room temperature. Then, 1.83 g (0.010 mole) of 2,6-dinitroaniline was added slowly and the solution was allowed to stand for 2 hours. Difluorammine (4.5 g) was generated from difluorourea and was allowed to reflux over the sulfuric-acid solution for 30 min. The mixture was drained onto 100 ml of ice. After the ice melted, a precipitate was filtered off, and the aqueous layer was extracted with 100 ml of methylene chloride. The precipitate was dissolved in 50 ml of methylene chloride, and the solution was dried over sodium sulfate and stripped of solvent to yield 0.90 g of 2,6-dinitroaniline, identified by its infrared spectrum. The extract solution of the aqueous layer was dried over sodium sulfate and the solvent was removed. Distillation of the residue (0.70 g) in a molecular still gave 0.20 g of a liquid at a pot temperature of 60°C at 0.025 mm Hg and 0.03 g at 80°C/25 mm Hg. Both materials solidified in the receivers, giving solids with m.p. values of 45 to 55°C and 58 to 63°C, respectively. Infrared spectra of the fractions were virtually identical, showing the absence of NH, OH, and carbonyl groups and the presence of strong peaks at 4.7 μ , indicating azide.

Anal. Calc'd for $C_6H_3N_3O_4$: C, 39.8; H, 1.65; N, 23.2.
Found: C, 40.48; H, 1.52; N, 23.9 (for first fraction).
C, 40.03; H, 1.37; N, 23.71 (for second fraction).

III. FLUOROAMMONIUM PERCHLORATE (V. Grakauskas)

This year's program has included a process study leading to the preparation of several pounds of fluoroammonium perchlorate (SAP). The process that was developed is based on the reaction between isopropyl N-fluorocarbamate and anhydrous

*Houben-Weyl, Methoden der Organischen Chemie, Stuttgart, Georg Thieme Verlag, Vol. X/3, Pt. I, p. 24 (1965).

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III Fluoroammonium Perchlorate (cont.)

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perchloric acid, and high-purity SAP is obtained quantitatively. The material is presently produced in lots of 70 to 140 g; pound quantities of the salt are now available.

A. DISCUSSION

The preparation of SAP from isopropyl N-fluorocarbamate and 70% aqueous perchloric acid* is a moderately good process when only few grams of the material is required. Scaling up appeared very complex, requiring large amounts of starting material and highly purified solvents. Furthermore, relatively elaborate remote-control, dry-box installations would have been required. Simplification of the method employed for the purification of crude SAP was the primary objective of the current work. Three different techniques had been used in the past: (1) sublimation, (2) crystallization from an ethyl acetate and chloroform mixture, and (3) chromatography on silica gel using an ethyl acetate solution of crude SAP.** Any one of these would have been too time-consuming in larger-scale preparations. Attempts to simplify purification led to a new process for SAP preparation.

Because SAP has limited solubility in 70% perchloric acid, it appeared that the material might be purified by crystallization from the acid. For evaluation of this method, the product resulting from the hydrolysis of isopropyl N-fluorocarbamate in an excess of 70% aqueous perchloric acid was partially concentrated until a portion of the SAP precipitated. The salt was collected and dried in vacuo; elemental analysis indicated that the material contained 0.5 to 1.2% of carbon. Repeated attempts to obtain carbon-free material in this manner failed. Although it is possible that improvements could have been realized, this approach was abandoned.

SAP has limited stability in 70% aqueous perchloric acid, and a considerable portion of the material is destroyed during its preparation from isopropyl N-fluorocarbamate. This decomposition may be responsible for side reactions leading to the formation of carbon-containing solids that coprecipitate with SAP and are difficult to remove during purification. In fact, when the sensitivity of SAP toward moisture is considered, it is surprising that the material can be obtained at all in the presence of 70% aqueous perchloric acid.

*Aerojet-General Report 2945 (Summary), October 1964, p. 34 (Confidential).

**Aerojet-General Report 3132 (Summary), October 1965, p. 22 (Confidential).

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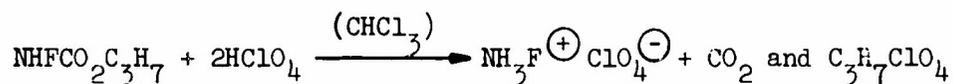
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III Fluoroammonium Perchlorate, A (cont.)

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The utilization of anhydrous perchloric acid for the preparation of SAP was considered in the past, but no experimental work was carried out because it was thought that aqueous perchloric acid would suffice. The unsatisfactory yield and 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 quantitatively. Elemental analysis and differential thermal analysis (DTA) showed that the product was of high purity. Preparation was repeated several times in the laboratory on a 5- to 10-g scale, and high-purity SAP was obtained practically quantitatively in all instances.

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



Isopropyl N-fluorocarbamate in chloroform solution is added to the anhydrous perchloric acid in chloroform solution. The rate of the reaction is followed by the rate of carbon dioxide evolution. The reaction is only mildly exothermic and the addition of the carbamate solution can 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 70 to 140 g. This entire larger-scale operation is carried out remotely.

The storage of SAP presents a problem. Earlier work showed that SAP could be stored for several months at ambient temperature in nickel containers.* These storability studies were conducted with small amounts of the material prepared by a different technique, and the results may or may not apply to the storability of SAP as it is now made. Attack on the walls of nickel containers was apparent when larger quantities of SAP (50 to 70 g) were stored at ambient temperature for 1 to 2 weeks. Pretreating of the nickel containers with HF appears to alleviate the corrosion problem.

* Aerojet-General Report 0235-01-23, August 1965, p. 15 (Confidential).

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

The preparation of SAP requires large quantities of isopropyl N-fluorocarbamate, which is obtained by the fluorination of isopropyl carbamate in acetonitrile. The crude isopropyl N-fluorocarbamate is contaminated with isopropyl carbamate and isopropyl N,N-difluorocarbamate. The latter can be readily removed from the mixture, but the separation of isopropyl N-fluorocarbamate from the starting material is difficult. The isolation of N-fluorocarbamate from this mixture by fractional distillation was found to be a tedious operation, and other potential purification routes were investigated. It was found that the mixture can be separated chromatographically on a silica column with methylene chloride as the solvent. The N-fluoro derivative can thus be readily eluted with the solvent and separated from isopropyl carbamate. This purification procedure, in conjunction with fractionation for the removal of difluorocarbamate, is now employed to obtain pound quantities of isopropyl N-fluorocarbamate.

B. EXPERIMENTAL

1. Preparation of SAP

a. With 70% Aqueous Perchloric Acid

To 2.8 g of 70% aqueous perchloric acid was added, dropwise with stirring at 25 to 30°C, 2.0 g of isopropyl N-fluorocarbamate over a period of 10 min. The reaction mixture was warmed to 35 to 40°C at the end of the carbamate addition and was allowed to stand at this temperature for 1 hour. The solution was then concentrated, at 40 to 45°C and a pressure of 50 μ Hg, to approximately 50% of its original volume. At this stage, some SAP precipitated and further removal of perchloric acid was discontinued. The reaction mixture

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was cooled to 20°C, and SAP was collected by filtration in a sintered glass funnel in a dry nitrogen atmosphere. The filter cake was transferred into a 10-ml round-bottomed flask, and residual perchloric acid was removed from the solid at 50 μ Hg and ambient temperature; the dry SAP amounted to 0.5 g.

Anal. Calc'd for NH_3FClO_4 : C, 0.0; H, 2.2; N, 10.2; F, 14.0.

Found: C, 0.7; H, 2.6; F, 13.1.

The above experiment was repeated with 7.0 ml of 70% perchloric acid and 5.0 g of isopropyl N-fluorocarbamate. The concentrated reaction mixture was allowed to stand at room temperature overnight and SAP was then isolated as above; weight, 1.7 g.

Anal. Found: C, 0.8; H, 2.7; F, 13.4.

b. With Anhydrous Perchloric Acid

Anhydrous perchloric acid was prepared from 70% aqueous perchloric acid and 20% fuming sulfuric acid following a procedure described by G. F. Smith.* To a solution of 6.9 g (0.0687 mole) of the acid in 70 ml of methylene chloride was added, from a dropping funnel at 20 to 22°C over a period of 40 minutes, a solution of 4.15 g (0.0343 mole) of isopropyl N-fluorocarbamate in 50 ml of methylene chloride. Slow gassing continued throughout and at the end of the carbamate addition. The reaction mixture was allowed to stand at 25°C for 5 hours, after which there was no noticeable evolution of gas. SAP was collected by filtration (sintered glass funnel, dry nitrogen atmosphere), and the filter cake was washed with three 20-ml portions of methylene chloride. The residual solvent was removed from the solid at a pressure of 0.2 mm Hg, and the stoppered funnel containing the material was transferred into a dry box; weight of SAP, 2.9 g (63% yield).

Anal. Found: C, 0.1; H, 2.5; N, 9.7; F, 14.0.

In this experiment it appeared that a weak complex was formed between SAP and the solvent; the removal of the residual methylene chloride from the product proceeded slowly and a relatively long period of pumping (60 min) was required. To avoid this possible complex formation, SAP was prepared in

* J. Am. Chem. Soc., **75**, 184 (1953).

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chloroform as follows: To a solution of 8.0 g (0.0762 mole) of anhydrous perchloric acid in 75 ml of chloroform (Baker's reagent grade, containing about 0.6% of methanol) was added, dropwise at 24 to 28°C, a solution of 4.6 g (0.0381 mole) of isopropyl N-fluorocarbamate in 12 ml of chloroform over a period of 20 min. At the end of the addition, the reaction mixture was warmed to 42 to 43°C and kept there until the evolution of carbon dioxide ceased (15 to 20 min). The reaction mixture was cooled to 20 to 25°C; SAP was collected by filtration and was washed with five 10-ml portions of chloroform. The vacuum-dried, crystalline, low-bulk-density material amounted to 4.7 g (91% yield).

Anal. Found: C, 0.16; H, 2.4; N, 9.7; F, 14.3.

The foregoing preparation was scaled up to 94 g (0.9353 mole) of anhydrous perchloric acid and 56.6 g (0.4676 mole) of isopropyl N-fluorocarbamate to give 63 g (quantitative yield) of low-bulk-density crystalline SAP.

Anal. Found: C, 0.1; H, 2.4; N, 10.1; F, 13.6.

Yet another run in chloroform under identical conditions yielded 64 g of SAP.

Anal. Found: C, 0.09; H, 2.1; F, 14.0.

The subsequent batches of SAP were obtained with remotely operated apparatus, which is being modified to arrive at the simplest and most efficient design. The final design will be presented in a special report on fluoroammonium perchlorate. The apparatus now consists of a well-shielded, three-necked, round-bottomed, 2-liter, glass flask equipped with a magnetic stirrer, a thermometer, and gas inlet and outlet tubes. The flask is surrounded by a trichloroethylene bath, which is used initially for cooling and subsequently for warming of the reactor. The bath is placed on the top of a remotely controlled hot-plate, magnetic-stirrer apparatus.

At the beginning of a run, the bath surrounding the reactor is kept at -80°C and anhydrous perchloric acid is distilled at reduced pressure from the generator and condensed in the reactor. The gas-inlet-tube joint of the reactor at this stage of the operation is used to receive the end of a condenser from the perchloric-acid generator. The gas-outlet tube of the reactor is connected through a -80°C safety trap to a vacuum pump. The perchloric-acid generator,

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containing a mixture of 70% perchloric and 20% fuming sulfuric acid, is weighed before and after the distillation; in this manner the weight of anhydrous perchloric acid distilled into the reactor is obtained. The perchloric-acid generator is now removed and replaced by an adapter that accommodates a dropping funnel containing chloroform (about 75 ml per 10 g of the acid). The reactor is warmed to -30 to -40°C and chloroform is introduced from the dropping funnel through the condenser. The reactor is now warmed to 20 to 25°C . The gas-outlet tube is connected to a wet-test meter, and isopropyl N-fluorocarbamate solution in chloroform (2 ml of chloroform per gram of carbamate) is added to the stirred perchloric-acid solution over a period of 20 to 40 min. After the carbamate addition, the reaction mixture is warmed to 40 to 45°C and the reaction is completed in 10 to 15 min. The reaction mixture is cooled to 20 to 25°C , and the thermometer in the center neck of the flask is replaced (remotely) by a filter stick. The solution is removed from the reactor by suction and replaced by fresh chloroform. At this stage, the reactor containing SAP suspension in chloroform is disconnected from the apparatus and the salt is collected by filtration in a sintered glass funnel. The filtration assembly is enclosed in a polyethylene bag, and a fast stream of dry nitrogen is passed through it during this operation. The filter cake is washed several times with chloroform, and the residual solvent is removed at 0.2 mm Hg. The closed funnel is now transferred to a dry box for the sampling and packaging of SAP.

This apparatus has been used to prepare SAP in lots of 70 to 140 g, and ten runs have successfully been completed. The SAP yields are practically quantitative in all cases, and the purity of the material corresponds to that observed in small-scale runs.

2. Purification of Isopropyl N-Fluorocarbamate

A solution of 1370 g (13.3 moles) of isopropyl carbamate in 9000 ml of acetonitrile was fluorinated at -10°C until approximately 16 moles of fluorine was consumed. The fluorination mixture was concentrated, first at 25 to $35^{\circ}\text{C}/25$ mm Hg and then at 20 to $25^{\circ}\text{C}/0.3$ mm Hg, to give 685 g of crude product. The material was diluted with 650 ml of methylene chloride, and the resulting solution was chromatographed on a silica column (2-1/4 in. ID and 5 ft 5 in. long) containing 1900 g of silica gel (Grace Chemical Division, desiccant activated, 28 to 200 mesh). Methylene chloride was used as the eluent.

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Isopropyl N-fluorocarbamate, 285 g (b.p. 46 to 48°C/0.3 to 0.5 mm Hg, N_D^{25} 1.3935), was isolated from the first six 500-ml fractions of methylene chloride solution by evaporation of the solvent, followed by distillation of the residual liquid. The distillation forerun contained some isopropanol.

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