Reactions of Aryldiazonium Fluoroborates with Isopropyl Fluorocarbamate and with Difluoramine[1]

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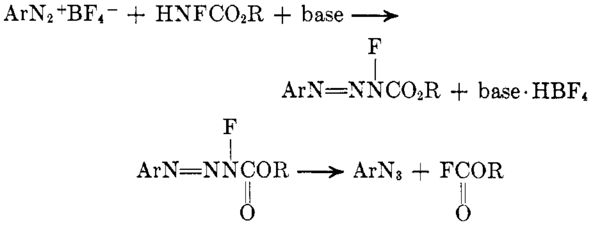
The reaction of isopropyl fluorocarbamate with aryldiazonium fluoroborates, in the presence of a mild base, gave aryl azides, isopropyl fluoroformate, and diisopropyl N-fluoriminodicarboxylate. Difluoramine and benzenediazonium fluoroborate gave *o*-fluorophenyl azide, *p*-fluorophenyl azide, and benzene. Difluoramine and 2,4,6-trimethylbenzenediazonium fluoroborate gave 2,4,6-trimethylphenyl azide. The products are rationalized on the basis of fluorotriazene intermediates.

Reactions of aryldiazonium ions with nucleophilic nitrogen species generally result in direct coupling products, as in the case of amines,[2] or nitrogen displacement products, as in the case of sodium nitrite.[3] Aromatic azides are formed from coupling products to nitrogen compounds with substituents that readily undergo α elimination, such as hydroxylamine,[4] arylhydrazines,[5] sulfonamides,[6] and chloramine.[7] It was of interest to determine the effect of NF groups on diazonium reactions. Alkyl fluorocarbamates have been shown to be sufficiently acidic to form anions under mild conditions;[8] so either coupling or nitrogen displacement might be expected. Difluoramine has not been reported to give a stable anion, but its hydrogen is sufficiently labile to undergo electrophilic substitution.[9]

No reaction took place when isopropyl fluorocarbamate was added to a suspension of an aryldiazonium fluoroborate in methylene chloride; a mild base was required to effect condensation. The addition of potassium fluoride to isopropyl fluorocarbamate and benzenediazonium fluoroborate in methyl chloride at 0–5° gave a 71.5% yield of phenyl azide, an 18% yield of diisopropyl N-fluoriminodicarboxylate, and isopropyl fluoroformate, which codistilled with the solvent. The addition of ammonia to the solvent fraction gave a 61% over-all yield of isopropyl carbamate. Higher reaction temperatures resulted in increases in yields of diisopropyl N-fluoriminodicarboxylate. Similarly, *o*-nitrobenzenediazonium fluoroborate, *m*-nitrobenzenediazonium fluoroborate, and *p*-nitrobenzenediazonium fluoroborate were converted into the corresponding azides in yields of 79–98%. The use of pyridine instead of potassium fluoride to remove fluoroboric acid gave the same results.

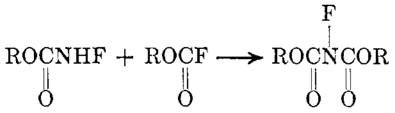
The formation of aryl azides by this reaction represents another example of diazonium coupling to a nitrogen compound with α elimination, the first such example in which an acyl halide is eliminated. The coupling product could lose fluoride and acylium ions or, alternatively, S$_N$2 attack by fluoride on the carbonyl carbon could give the fluoroformate and the N–F anion which would lose fluoride to give the azide (eq 1).



$$\mathrm{ArN_2^+BF_4^-} + \mathrm{HNFCO_2R} + \text{base} \longrightarrow \mathrm{ArN{=}N\overset{F}{N}CO_2R} + \text{base}\cdot\mathrm{HBF_4} \quad (1)$$

$$\mathrm{ArN{=}N\overset{F}{N}\underset{O}{C}OR} \longrightarrow \mathrm{ArN_3} + \mathrm{F\underset{O}{C}OR}$$

Diisopropyl N-fluoriminodicarboxylate was most likely formed from the reaction of isopropyl fluoroformate with isopropyl fluorocarbamate. The acylation of N-fluorocarbamates with chloroformates has been reported[8] (eq 2).



$$\mathrm{RO\underset{O}{C}NHF} + \mathrm{RO\underset{O}{C}F} \longrightarrow \mathrm{RO\underset{O}{C}\overset{F}{N}\underset{O}{C}OR} \quad (2)$$

Benzenediazonium fluoroborate, which has low solubility in common solvents, including water, was found to be very soluble in liquid difluoramine at its boiling point (−23°). No reaction took place, and the diazonium salt was recovered quantitatively when the difluoramine was removed. However, the addition of pyridine or potassium fluoride to remove fluoroboric acid resulted in the formation of *o*-fluorophenyl azide, *p*-fluorophenyl azide, and benzene. These azides, as well as the *meta* isomer, were synthesized independently by the nitrosation of the corresponding fluorophenylhydrazines and comparison of the fluorine nmr spectra of the three with that of the product showed that only the latter was absent. Yields in the difluoramine reaction were variable, and considerable amounts of tars were formed. In several instances two unidentified products were formed with ^{19}F signals indicative of NF compounds: a 1:1:1 triplet at ϕ^* −32.5[10] and a broadened singlet at ϕ^* −26.2.

Sodium fluoride was not sufficiently basic to effect the condensation of the diazonium salt with difluoramine, and the starting material was recovered. Cesium fluoride, on the other hand, gave violent decomposition even when methylene chloride was added as a diluent.

o-Fluorophenyl azide and *p*-fluorophenyl azide could be formed from the expected coupling product, 1-phenyl-3,3-difluorotriazene, by loss of fluoride ion to give a resonance-stabilized cation having carbonium

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[1] This work was supported by the Office of Naval Research and the Advanced Research Projects Agency.

[2] P. Griess, *Ann.*, **121**, 258 (1862); H. Von Pechmann and L. Frobenius, *Ber.*, **28**, 170 (1895); B. F. Day, T. W. Campbell, and G. M. Coppinger, *J. Amer. Chem. Soc.*, **73**, 4687 (1951).

[3] E. R. Ward, C. D. Johnston, and J. G. Hawkins, *J. Chem. Soc.*, 894 (1960).

[4] J. Mai, *Ber.*, **25**, 372 (1892).

[5] T. Curtius, *ibid.*, **26**, 1263 (1893); E. Fischer, *Ann.*, **190**, 67 (1878); P. Griess, *Ber.*, **9**, 1659 (1876).

[6] P. K. Dutt, H. R. Whitehead, and A. Wormall, *J. Chem. Soc.*, **119**, 2088 (1921); A. Key and P. V. Dutt, *ibid.*, 2035 (1928); H. Bretschneider and H. Rager, *Monatsh. Chem.*, **81**, 970 (1950).

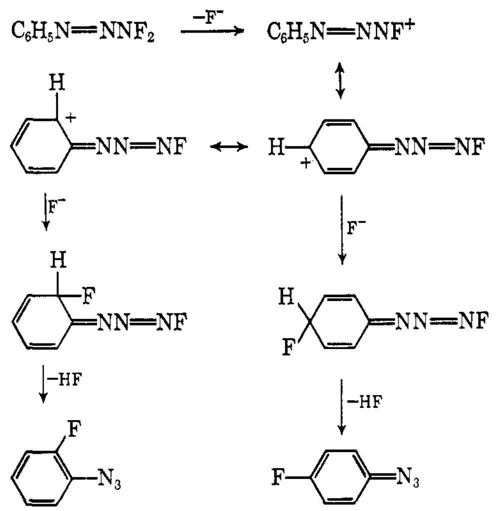
[7] M. O. Forster, *J. Chem. Soc.*, **107**, 260 (1915).

[8] V. Grakauskas, Third International Fluorine Symposium, Munich, Sept 1965.

[9] W. H. Graham and J. P. Freeman, *J. Amer. Chem. Soc.*, **89**, 716 (1967).

[10] For definition of ϕ^*, see G. V. D. Tiers and G. Filipovich, *J. Phys. Chem.*, **63**, 761 (1959).

ion character at the *ortho* and *para* positions. The addition of fluoride at these positions would give semiquinoid intermediates which would give the observed fluoro azides by the elimination of HF. The absence of the *meta* isomer is consistent with this mechanism (eq 3).



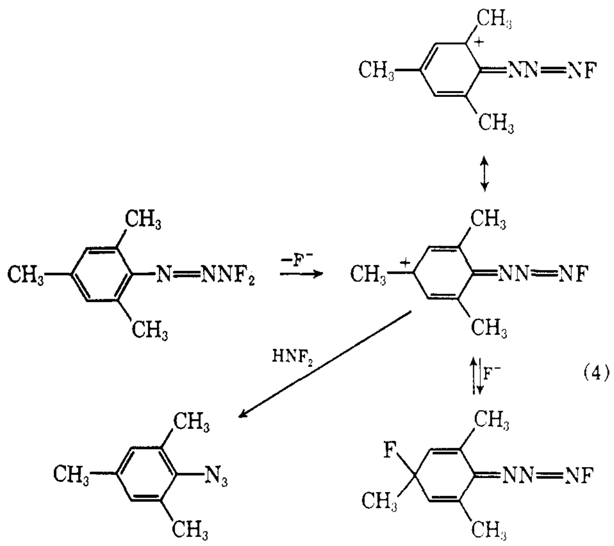
(3)

Diazonium salt reductions generally take place by a homolytic mechanism,[11] and the above difluorotriazene would be expected to react readily in this manner by loss of the stable[12] difluoramino radical. The resulting diazoaryl or aryl radicals could abstract hydrogen from difluoramine to give benzene.

Blocking the *ortho* and *para* positions of the diazonium salt with methyls should alter the above path in two ways. The diazonium coupling product should lose fluoride more readily because of methyl stabilization of positive charge in the ring. Homolytic decomposition should therefore consume a smaller portion of the intermediate. However, addition of fluoride ion to *ortho* or *para* positions in the cation cannot lead to fluoro azides without the rupture of a C–C bond; so this step should be reversible.

The reaction of 2,4,6-trimethylbenzenediazonium fluoroborate with difluoramine in the presence of potassium fluoride was found to give an 86% yield of 2,4,6-trimethylphenyl azide and a trace of mesitylene. The azide could not be distilled without decomposition, but an analytical sample for comparison was prepared independently from the diazonium salt and sodium azide. The formation of 2,4,6-trimethylphenyl azide could take place by loss of fluoride from the triazene, followed by aromatization by loss of electropositive fluorine to an available fluorination substrate, *i.e.*, difluoramine. An example of the fluorination of an anion by a neutral difluoramino compound has been reported[13] (eq 4).

The products obtained in the reactions of diazonium salts with isopropyl fluorocarbamate and with difluoramine thus indicate that nitrogen coupling takes place to give unstable fluorotriazenes, which can react further by a variety of mechanisms, depending on substituents.



(4)

Experimental Section

Reaction of Isopropyl Fluorocarbamate with Benzenediazonium Fluoroborate.—Benzenediazonium fluoroborate[14] (5.73 g, 0.030 mol) was added to a solution of 3.63 g (0.030 mol) of isopropyl fluorocarbamate[8] in 30 ml of methylene chloride. The resulting slurry was cooled to 0°, and 6.0 g (0.104 mol) of potassium fluoride was added in small portions over a 10-min period. After the mixture was stirred an additional 2.5 hr at 0–5°, it was pressure filtered, and the solids were washed with three 10-ml portions of methylene chloride. The solvent was removed from the combined methylene chloride solutions by distillation [25° (300 mm)], and the residue was vacuum distilled to give 2.55 g (0.0214 mol, 71.3% yield) of phenyl azide, bp 49–50° (5 mm),[15] and 1.13 g (0.0055 mol, 18% yield) of diisopropyl N-fluoriminodicarboxylate, bp 68° (0.02 mm).

Anal. Calcd for $C_8H_{14}NO_4F$: C, 46.38; H, 6.77; N, 6.77; F, 9.19. Found: C, 46.14; H, 6.92; N, 7.01; F, 9.22.

The ^{19}F nmr spectrum consisted of a single peak at ϕ^* 68.7. The proton spectrum showed only isopropyl groups (doublet at δ 1.38 and septet at δ 5.10).

Isopropyl fluoroformate codistilled with the solvent, and a sample was isolated by gas chromatography (10 × 0.25 in. column of 5% Carbowax 4000 on Fluoropak 80 at 60°).

Anal. Calcd 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 ^{19}F nmr spectrum consisted of an octet (J = 1.5 cps), with outer members barely detectable over background. Fluorine spectra of other fluoroformates have been reported in this region.[16] The proton spectrum consisted of a doublet (J_{HH} = 6.3 cps) of doublets (J_{HF} = 1.5 cps) at δ 1.41 for the methyls and a septet (J_{HH} = 6.3 cps) of doublets (J_{HF} = 1.5 cps) for the CH. Anhydrous ammonia was bubbled through the methylene chloride solution for several minutes. The solvent was removed under vacuum to give 1.87 g (0.0182 mol, 61% yield) of isopropyl carbamate, mp 93°.[17]

Reaction of Isopropyl Fluorocarbamate with Nitrobenzenediazonium Fluoroborates.—Potassium fluoride (1.2 g, 0.020 mol) was added during a 10-min period with stirring to a mixture of 10 ml of methylene chloride, 2.37 g (0.01 mol) of *o*-nitrobenzenediazonium fluoroborate, and 1.21 g (0.01 mol) of isopropyl fluorocarbamate at 0°. 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

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[11] P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966; H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961.

[12] F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, **83**, 3043 (1961).

[13] R. E. Banks and O. E. Williamson, *Chem. Ind.* (London), 1864 (1964).

[14] D. T. Flood, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 295.

[15] R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 710.

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

[17] J. Thiele and F. Dent, *Ann.*, **302**, 269 (1898).

ml of methylene chloride. Solvent was removed from the combined methylene chloride solutions under vacuum. The residue, an oil, was crystallized from pentane to give 1.61 g (98% yield) of *o*-nitrophenyl azide, mp 51–52° (lit.[18] mp 53°).

The identical procedure with *m*-nitrobenzenediazonium fluoroborate gave 1.40 g (85% yield) of *m*-nitrophenyl azide, mp 51–53° (lit.[19] mp 55°). Similarly, *p*-nitrobenzenediazonium fluoroborate gave 1.3 g (79% yield) of *p*-nitrophenyl azide, mp 68° (lit.[20] mp 70°). 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 mol) of pyridine was added, dropwise with stirring at 0–5°, to a stirred mixture of 3.63 g (0.03 mol) of isopropyl fluorocarbamate, 5.73 g (0.0242 mol) of *p*-nitrobenzenediazonium fluoroborate, and 30 ml of methylene chloride. The mixture was kept at 0–5°, with stirring, for 30 min. A precipitate, identified as pyridine fluoroborate 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, mp 55–60°. Recrystallization from methylene chloride and pentane gave 2.5 g (63% yield) of product, mp 70°.

Starting with *o*-nitrobenzenediazonium fluoroborate, the same procedure gave 4.8 g of crude product, mp 25–40°. Recrystallization as above gave 2.2 g (55% yield) of *o*-nitrophenyl azide, mp 52–53°.

Fluorophenyl Azides.—Sodium nitrite (0.43 g, 0.0062 mol) was added dropwise to a stirred suspension of 1.0 g (0.0062 mol) of *p*-fluorophenylhydrazine hydrochloride in 5 ml of water while the reaction temperature was held at 0–5°. 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 ^{19}F nmr spectrum showed a "quintet" at ϕ^* 118.1.

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 ^{19}F signal of *o*-fluorophenyl azide was an almost symmetrical multiplet at ϕ^* 127.5. That of *m*-fluorophenyl azide exhibited a general quartet profile with additional splitting of the inner members; its position was ϕ^* 112.0. The infrared spectra showed strong azide bands at 4.7 μ.

Reaction of Benzenediazonium Fluoroborate with Difluoramine.—Difluoramine was generated as described previously.[21] Explosion shields and remote handling devices are required, and air must be excluded from the system.

Pyridine (0.62 g, 0.0104 mol) was added dropwise, with stirring, to a mixture of 2.0 g (0.0104 mol) of benzenediazonium fluoroborate and 4.5 g of difluoramine at −40°. The reaction temperature was allowed to rise to −10° over a 1-hr 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° receiver as the pressure was gradually reduced to 100 mm. The pressure was then lowered to 0.01 mm to yield 0.1 g of distillate. The ^{19}F nmr spectrum showed *p*-fluorophenyl azide (ϕ 118 ppm) and *o*-fluorophenyl azide (ϕ^* 127 ppm) in a ratio of 62:102.

In two of six similar experiments, two additional ^{19}F signals were observed, a 1:1:1 triplet (J = 46 cps) at ϕ^* −32.5 and a broadened singlet at ϕ^* −26.2. Benzene was also formed in variable amounts.

The use of potassium fluoride instead of pyridine gave similar results. Sodium fluoride, however, did not effect condensation, and the benzenediazonium fluoroborate was recovered quantitatively. The use of cesium fluoride resulted in an explosion when no diluent was used and a fume-off when methylene chloride was added.

Reaction of 2,4,6-Trimethylbenzenediazonium Fluoroborate with Difluoramine.—To a solution of 2.34 g (0.01 mol) of 2,4,6-trimethylbenzenediazonium fluoroborate[22] in 3 ml of refluxing difluoramine, 2.0 g (0.034 mol) of potassium fluoride was introduced by means of an addition tube. The mixture was stirred under reflux for 1.5 hr, 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 2,4,6-trimethylphenyl azide (86% yield) containing a trace of 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 mol) of sodium azide in 5 ml of water to a solution of 1.0 g (0.0043 mol) of 2,4,6-trimethylbenzenediazonium fluoroborate in 20 ml of water at 5°. 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. Calcd 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 μ 3.40 (w), 4.72 (s), 6.2 (w), 6.8 (m), 7.6 (m), 7.8 (m), 9.1 (w), and 11.7 (m).

Registry No.—Isopropyl fluorocarbamate, 17603-82-6; difluoramine, 10405-27-3; diisopropyl N-fluoriminodicarboxylate, 17603-84-8; isopropyl fluoroformate, 461-71-2; 2,4,6-trimethylphenyl azide, 14213-00-4.

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[18] T. Zinoke and O. Schwarz, *Ann.*, **307**, 35 (1899).

[19] E. Noelting, E. Grandmougin, and O. Michel, *Ber.*, **25**, 3338 (1892).

[20] H. Rupe and K. V. Majewski, *ibid.*, **33**, 3408 (1900).

[21] V. Grakauskas, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p 23M; K. Baum, *J. Org. Chem.*, **32**, 3648 (1967).

[22] F. Brown, J. M. A. deBruyne, and P. Gross, *J. Amer. Chem. Soc.*, **56**, 1291 (1934).