The solution was refluxed for 3 days, but the reaction was not complete on the basis of a qualitative examination by ultraviolet spectroscopy. Additional sodium (6.9 g, 0.30 g-atom) in 200 ml of 2-propanol was added and reflux was continued another 4 days. The reaction was cooled to room temperature and filtered, and the filtrate was concentrated to a small volume. Water (200 ml) and ether (200 ml) were added and the mixture was neutralized with dilute hydrochloric acid. The ether layer was separated, washed with water, dried over magnesium sulfate, and distilled to give 3.7 g (27%) of product; bp 92–97° (75–78 mm); λ_{max} at 272 mμ in 95% ethanol.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.85; H, 8.04; N, 10.40.

2-Alkoxypyridines by Alkylation of 2-Pyridone. 2-Isopropyloxypyridine.—2-Pyridone (5.1 g, 0.053 mole), silver carbonate (7.5 g, 0.027 mole), and isopropyl iodide (8.8 g, 0.052 mole) were stirred for 24 hr in 60 ml of pentane at 42° in the dark. The mixture was cooled in an ice bath for 0.5 hr and filtered from silver salts.

The filtrate was washed with 50 ml of 1% sodium bicarbonate solution and then twice with 25-ml portions of water. The pentane was removed at atmospheric pressure, except for the last traces which were removed under vacuum. The remaining pale yellow liquid (5.4 g, 76%) was 95% (area) 2-isopropyloxypyridine by vpc. Chromatographically pure product was obtained by distillation, bp 90–92° (155 mm).

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.02; H, 8.07; N, 10.27.

This procedure was also used to prepare **2-methoxy-** and **2-benzyloxypyridine** in 57 and 78% yield, respectively, after distillation. All three products were chromatographically pure and were identified by comparison with authentic samples (infrared and ultraviolet spectra, boiling points, and vpc retention times were compared).

Rate Studies.—Reactions were run in dimethylformamide dried over Linde Molecular Sieves (Type 13X) and products were analyzed by vpc as noted previously. Table V summarizes the results of this study. Figures 1 and 2 show the second-order rate plots for ethylation and isopropylation. Methylation and benzylation were too rapid for study by this technique. Isopropylation was followed only to 30–36% completion, but corresponding first-order plots were curved lines.

Notes

Organic Fluoronitrogens. VIII.[1] Hydrolytic Reactions of Tetrafluoroformamidine and Pentafluoroguanidine

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Recently the synthesis and properties of tetrafluoroformamidine and the closely related compound, pentafluoroguanidine, were disclosed.[1,2] Unlike many saturated fluoronitrogens, these materials are quite sensitive to moisture and therefore we have surveyed their reactions with water, aqueous base, and strong acids.

The reactions of both tetrafluoroformamidine and pentafluoroguanidine with alkali are rapid and exothermic. Frequent explosions occurred during the contacting of excess gaseous pentafluoroguanidine with 5 *N* or more concentrated solutions of sodium hydroxide. However, this reaction can be controlled by gradually exposing the gaseous fluoronitrogen to a well-stirred solution of excess alkali. Tetrafluoroformamidine yields mostly nitrogen as a gaseous product from 5 *N* or more concentrated alkali (eq 1). On

$$F_2NCF{=}NF + 6OH^- \rightarrow CO_3^{2-} + 4F^- + 3H_2O + N_2 \quad (1)$$

the other hand, the major gaseous products from pentafluoroguanidine include nitrogen, nitrous oxide, and the two isomers of difluorodiazine. The difluoramino anion[3] is a probable intermediate (eq 2–4).

$$(F_2N)_2C{=}NF + 6OH^- \rightarrow CO_3^{2-} + 3F^- + 3H_2O + N_2 + [NF_2^-] \quad (2)$$

$$2[NF_2^-] \rightarrow N_2F_2 + 2F^- \quad (3)$$

$$2[NF_2^-] + 2OH^- \rightarrow N_2O + H_2O + 4F^- \quad (4)$$

The reactions of tetrafluoroformamidine and pentafluoroguanidine with concentrated sulfuric acid are relatively slow (eq 5 and 6). Under our experimental conditions, a period of about 2 days is required for a complete reaction. The oxidation numbers of the nitrogen atoms in the difluoramino and fluorimino groups are preserved in the hydrolysis products, difluoramine and hydroxylammonium ion. The hydrofluoric acid produced reacts with the glass reaction vessel and appears in the gas phase as silicon tetrafluoride. In view of the over-all dehydrating conditions, it is quite possible that the hydroxylammonium species is originally present as hydroxylamine O-sulfonic acid. Thus, the diluted solution purged free of difluoramine oxidizes iodide as would be expected of this derivative. However, after boiling the diluted solution and removing the excess sulfuric acid by chloride anion exchange, hydroxylammonium chloride is the isolated product.

$$F_2NCF{=}NF + 3H_2O + H_2SO_4 \rightarrow HNF_2 + CO_2 + 2HF + HONH_3^+ + HSO_4^- \quad (5)$$

$$(F_2N)_2C{=}NF + 3H_2O + H_2SO_4 \rightarrow 2HNF_2 + CO_2 + HF + HONH_3^+ + HSO_4^- \quad (6)$$

In water tetrafluoroformamidine and pentafluoroguanidine hydrolyze completely within a few hours. The distribution of the hydrolysis products from tetrafluoroformamidine is shown in Table I. The carbon is converted entirely to carbon dioxide. Difluoramine and hydroxylammonium ion (or its precursor) are produced in equimolar amounts originally, but much of the latter disproportionates to ammonium ion and nitrogen. Difluoramine and hydroxylammonium ion can also react to form nitrogen gas (eq 7); this reaction was demonstrated independently by combining the two reactants in aqueous solution at room temperature. The addition of sulfuric acid to a final concentration of 1 *N* reduces the yield of nitrogen from

$$HNF_2 + HONH_3^+ \rightarrow N_2 + 2HF + H^+ + H_2O \quad (7)$$

(1) Previous paper in this series: R. J. Koshar, D. R. Husted, and C. D. Wright, *J. Org. Chem.*, **32**, 3859 (1967).

(2) R. A. Davis, J. L. Kroon, and D. A. Rausch, *ibid.*, **32**, 1662 (1967).

(3) The existence of the difluoramino anion and its scheme of hydrolysis have been reported: K. J. Martin, *J. Am. Chem. Soc.*, **87**, 394 (1965).

TABLE I
DISTRIBUTION OF THE MAJOR PRODUCTS FROM THE HYDROLYSIS OF TETRAFLUOROFORMAMIDINE

Product	Yield, moles of product per mole of $F_2NCF{=}NF$
CO_2	1.0
HNF_2	0.4
N_2	0.7
NH_4F	0.1
$HONH_3^+F^-$	0.1
HF	3.0

the tetrafluoroformamidine–water reaction to 50 mole %.

Some unexpected products result from the reactions of tetrafluoroformamidine and pentafluoroguanidine with strong acids other than sulfuric acid. Bis(difluoramino)dichloromethane is produced from the relatively rapid reaction between *agua regia* and pentafluoroguanidine. The other products from this reaction include a mixture of nitrogen oxides, hydrofluoric acid, and carbon dioxide. Treatment of the final reaction mixture with an excess of aqueous alkali leaves only bis(difluoramino)dichloromethane and nitrous oxide in the gaseous phase. The nitrous oxide is readily removed by fractional distillation. Although some properties of bis(difluoramino)dichloromethane have been disclosed previously,[4] the reaction described here is the first synthetic approach to this compound to be reported.

With concentrated hydrochloric acid, tetrafluoroformamidine yields chlorodifluoramine, carbon dioxide, hydrofluoric acid, and other products. High yields of chlorodifluoramine result from the combination of pentafluoroguanidine and hydrochloric acid at room temperature. Concentrated nitric acid oxidizes the fluoronitrogen functions of pentafluoroguanidine to a mixture of nitrogen oxides; carbon dioxide and hydrofluoric acid are also produced.

Experimental Section

Materials.—Tetrafluoroformamidine and pentafluoroguanidine were prepared according to the method of Koshar, Husted, and Wright[1] and purified by gas chromatography with the column described previously.[5] The other materials used were reagent grade.

Safety Precautions.—Because tetrafluoroformamidine and pentafluoroguanidine tend to explode upon impact, freezing, or contact with alkali, the safety precautions recommended by Koshar, Husted, and Meiklejohn[6] were closely followed.

Method of Hydrolysis.—The reactions were carried out at 25° in a 10-ml erlenmeyer flask attached to a calibrated vacuum manifold (*ca.* 20 ml) through a glass gas sampling loop (Figure 1). Samples of the fluoronitrogen, usually 0.1 mmole, were measured manometrically and condensed into the previously evacuated reactor containing 1.0 ml of water, acid, or base. The mixtures were allowed to warm to room temperature and were stirred magnetically.

Methods of Analysis.—The progress of the reactions was followed by gas chromatography. A series of 0.2-ml samples of the gaseous phase was analyzed with a modified Fisher gas partitioner equipped with a single 12-ft column of 3M Brand inert fluorochemical FC-43 on an acid-washed Celite support. The relative molar responses of the various gases to detection by thermal conductivity were determined empirically: N_2 (1.00), CO_2 (1.19), $F_2NCF{=}NF$ (1.85), and $(F_2N)_2C{=}NF$ (2.22). At the completion of each reaction, the gaseous phase was also analyzed with the infrared and mass spectrometric equipment described previously.[6] Difluoramine was also determined iodometrically by the method of Lawton and Weber.[7] Hydroxylammonium and ammonium ions were separated from fluoride, sulfate, fluorosilicate, and fluoroborate ions by percolating the diluted, hydrolyzed solution over a bed of Bio-Rad AG1X4 (Cl^-, 100–200 mesh). The resulting chloride salts were identified by their infrared spectra. Hydroxylammonium ion was determined by bromate oxidation, and fluoride ion by the classical thorium nitrate titration.

(4) R. L. Rebertus, J. J. McBrady, and J. G. Gagnon, *J. Org. Chem.*, **32**, 1944 (1967).
(5) R. A. Mitsch, *J. Heterocyclic Chem.*, **3**, 245 (1966).
(6) R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *J. Org. Chem.*, **31**, 4232 (1966).

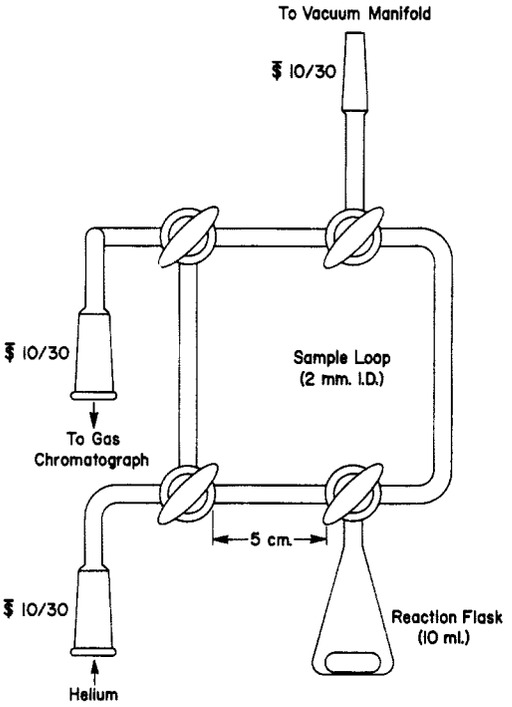

Figure 1.—Reaction vessel and sampling loop.

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(7) E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **81**, 4755 (1959).

Organic Fluoronitrogens. IX.[1] Oxidation–Reduction Reactions of Tris(difluoramino)fluoromethane, Tetrafluoroformamidine, and Pentafluoroguanidine

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Recently several new organic fluoronitrogens were disclosed.[2-4] The synthetic methods reported lead to

(1) Previous publication in this series: R. L. Rebertus and B. W. Nippoldt, *J. Org. Chem.*, **32**, 4044 (1967).
(2) R. A. Davis, J. L. Kroon, and D. A. Rausch, *ibid.*, **32**, 1662 (1967).
(3) R. J. Koshar, D. R. Husted, and C. D. Wright, *ibid.*, **32**, 3859 (1967).
(4) R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *ibid.*, **31**, 4232 (1966).