REPORT NO. 5015-2 (ANNUAL)

PERIOD COVERED: 1 DECEMBER 1968 THROUGH 1 DECEMBER 1969

RESEARCH IN NF COMPOUNDS

A Report on Work Sponsored By

THE OFFICE OF NAVAL RESEARCH

CONTRACT N00014-69-C-0015

JANUARY 1970

COPY NO. 10

ENVIRONMENTAL SYSTEMS DIVISION

AEROJET-GENERAL CORPORATION
EL MONTE, CALIFORNIA

January 1970

Report No. 5015-2
(Annual)

RESEARCH IN NF COMPOUNDS

By

K. Baum and V. Grakauskas

Analytical Support: K. Inouye and L. A. Maucieri

A Report on Work Sponsored By

THE OFFICE OF NAVAL RESEARCH

Contract N00014-69-C-0015

AEROJET-GENERAL CORPORATION

A Subsidiary of The General Tire & Rubber Company

ABSTRACT

Gem-diperchlorates were obtained by the reaction of ketones with anhydrous perchloric acid in halogenated solvents. Cyclohexene was reduced to cyclohexane by perchloric acid in chloroform.

Isopropyl chlorofluorocarbamate and bromofluorocarbamate added to olefins and acted as halogenating agents toward hydrocarbons by free radical chain mechanisms involving fluoraminocarboalkoxy free radicals. Isopropyl fluorocarbamate and mercuric oxide gave bis(carboisopropoxyfluoramino)mercury. The latter was found to add to olefins.

The following phases of earlier research were completed and the work was assembled in the form of manuscripts: (1) Direct Fluorination of Ureas, (2) Direct Fluorination of Amides, and (3) Synthesis of α,α-Dinitro-N'-fluorodiimide N-Oxides.

CONTRACT FULFILLMENT STATEMENT

This annual technical report is submitted in partial fulfillment of the contract and covers the period from 1 December 1968 through 1 December 1969.

AEROJET-GENERAL CORPORATION

W. P. Knight, Manager
Special Projects

L. R. Rapp, Manager
Research & Technology Department

CONTENTS

INTRODUCTION

The objectives of this program are to develop synthesis methods for new types of high-energy compounds and to increase our understanding of the processes involved. During the past year, emphasis was placed on the completion of areas of research that were investigated on the preceding contract, Nonr 2655(00), and on the preparation of manuscripts. Three manuscripts covering earlier work are presented as appendices: A, "Direct Fluorination of Ureas"; B, "Direct Fluorination of Amides"; and C, "Synthesis of α,α-Dinitro-N'-fluorodiimide N-Oxides".

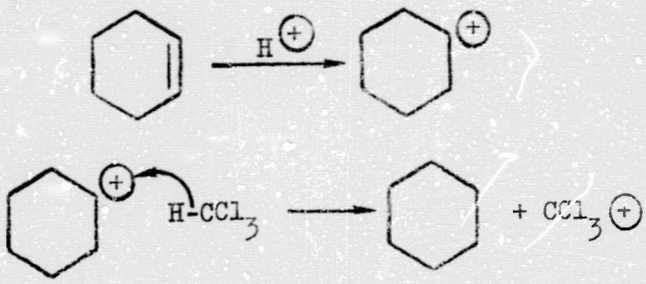
In the preceding semiannual report (Aerojet Report 5015-1, May 1969) three manuscripts were included: "Substituent Constants of Difluoraminoalkyl and Gem-bis(difluoramino)alkyl Groups," "Direct Fluorination of Secondary Nitronate Salts," and "Michael Reactions of 2-Fluoro-2,2-dinitroethanol and 2,2-Dinitropropanol with Olefinic and Acetylenic Acceptors."

New work comprising the body of this report deals with chemistry of perchloric acid and of fluorocarbamates.

Perchloric Acid Chemistry
(K. Baum)

The acid strength of a solution is limited by the acidity of the conjugate acid of the solvent. For this reason, perchloric acid is a stronger acid in acetic acid than in aqueous solution.[1] Perchloric acid is soluble in chloroform and similar solvents which have very low basicity.[2] Such solutions should therefore possess "superacid" properties, while at the same time providing a medium of low ionizing power. On the other hand, the strongly acidic media which are being widely investigated, mainly combinations of fluosulfonic acid, sulfur dioxide, and antimony pentafluoride, are also strongly ionizing media. Solutions of anhydrous perchloric acid in chloroform and methylene chloride have been used to prepare fluorammonium perchlorate[3] from fluorocarbamates under much milder conditions than are required with commercially available 70% perchloric acid. Novel chemical reactivity of perchloric acid in halogenated solvents with organic compounds could result from enhanced acidity of the perchloric acid as well as lack of solvent stabilization of the resulting cations.

Tauber and Eastham[4] studied the reaction of perchloric acid in ethylene dichloride with 2-butene, but could not identify the products. Nmr spectroscopy now provides a convenient tool for studying reactions of this type. For simplicity, we selected cyclohexene as the olefin and chloroform as the solvent. The nmr spectrum of a solution formed by adding cyclohexene to an excess of anhydrous perchloric acid in chloroform showed cyclohexane as the principal product. Other products have not yet been identified. Perchloric acid in chloroform thus acts as a reducing agent toward the olefin. Apparently, the initially formed carbonium ion abstracts hydride from the solvent. Similar reductions with trifluoroacetic acid have been reported with silanes or tertiary hydrocarbons as hydride sources.[5]



Reactions of ketones and aldehydes with perchloric acid in chloroform or methylene chloride were also studied. The addition of acetone to an excess of the acid in chloroform resulted after several minutes in the separation of a heavy liquid. The nmr spectrum of the chloroform layer showed only a single signal other than that of the solvent, a sharp singlet at δ 2.59. Perchloric acid, which appears at δ 8-12 (depending on concentration) was absent. The infrared spectrum showed major peaks at 9.0 and 9.2 μ. Removal of the solvent from a similarly prepared solution gave a slightly yellow liquid which gave analytical data consistent with 2,2-propanediperchlorate.

Anal. Calcd for $C_3H_6O_8Cl_2$: C, 14.9; H, 2.5. Found: C, 14.45; H, 2.72.

The lower layer contained a considerable amount of perchloric acid. When the reaction was carried out with a stoichiometric amount of perchloric acid using methylene chloride as the solvent, no separate layer formed but the same product was formed. The material could be distilled at 52° (0.1 mm), and the nmr spectrum of the distillate was identical with that of the chloroform solution. DTA showed an exotherm starting at 85° with a peak at 159°, followed by a second exotherm starting at 202° with explosion at 250°. The diperchlorate was very sensitive to moisture, and drybox handling was required for analysis.

The same reaction took place with 2-butanone and excess perchloric acid in chloroform. A heavy liquid separated, and stripping the chloroform layer gave a pale yellow liquid which analyzed as the diperchlorate.

Anal. Calcd for $C_4H_8Cl_2O_8$: C, 18.84; H, 3.14. Found: C, 19.02; H, 3.75.

Preliminary screening experiments were conducted to determine if similar reactions occur with aldehydes. The reaction of trioxane with perchloric acid in chloroform gave a solid precipitate, and the nmr spectrum of the chloroform solution showed perchloric acid (δ 9.86) and three singlets at δ 5.78, 5.73, and 5.16 with relative areas of 10:2:1. The precipitate was partially soluble in methylene chloride and the solution showed singlets at δ 5.74 and 4.66. Butyraldehyde gave a separate liquid layer in the perchloric acid reaction, but the nmr spectrum of the chloroform solution indicated that the reaction was incomplete.

REFERENCES

1. G. Schwarzenbach and P. Stensby, Helv. Chim. Acta., 42, 2342 (1959).

2. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., New York, N.Y., 1946, p. 380.

3. V. Grakauskas, A. H. Remanick, and K. Baum, J. Amer. Chem. Soc., 90, 3839 (1968).

4. S. J. Tauber and A. M. Eastham, J. Am. Chem. Soc., 82, 4888 (1960).

5. D. V. Kursanov, Z. N. Parnes, G. I. Bassova, N. M. Loim, and V. E. Zdanovich, Tetrahedron, 1967, 2235.

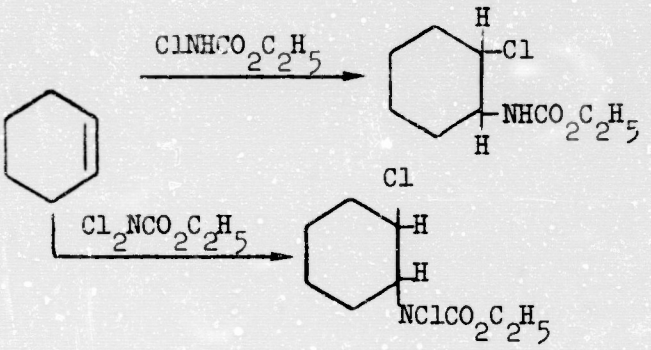
6. A. F. Smith, J. Amer. Chem. Soc., 75, 184 (1953).

Reactions of Fluorocarbamates

(V. Grakauskas)

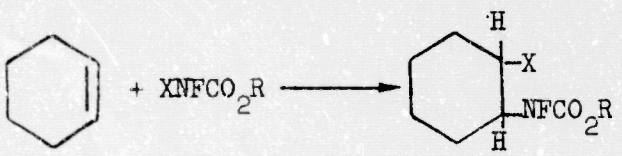
The synthesis of N-chloro-N-fluorocarbamates and N-bromo-N-fluorocarbamates was reported several years ago.[1] The latter represents the only reported compound containing bromine and fluorine on a nitrogen atom, and few organic N-chloro-N-fluoramines derivatives are known. The chemical reactions of these unique NF compounds have now been investigated as potential sources of simple NF radicals and ions.

The additions of chlorourethane and dichlorourethane to cyclohexene were reported[2] to give 2-chlorocyclohexylurethane and 2-chlorocyclohexyl-N-chlorourethane, respectively, by free radical mechanisms.



Similar reactions of halofluorocarbamates would involve fluorocarbamyl radicals as intermediates. No NF radicals other than $\cdot NF_2$ have been identified previously.

Isopropyl chlorofluorocarbamate and isopropyl bromofluorocarbamate reacted with cyclohexene to give 2-chlorocyclohexylfluorocarbamate and 2-bromocyclohexylfluorocarbamate, respectively, in 85-95% yield:



X = Cl,Br; R = i-C_3H_7

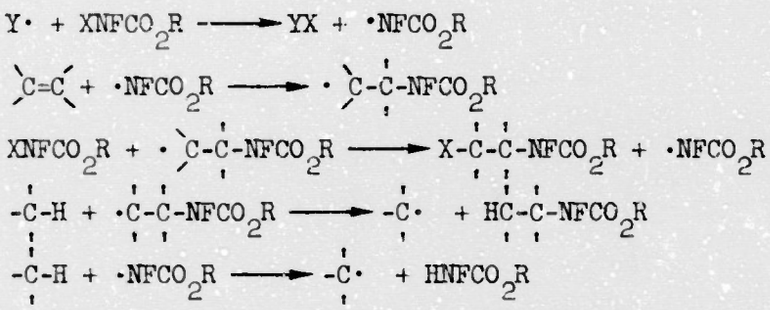
The reaction of bromofluorocarbamate was instantaneous, and that of chlorofluorocarbamate required several hours for completion. In both cases small amounts of isopropyl fluorocarbamate and isopropyl N-cyclohexyl-N-fluorocarbamate were also formed. These sideproducts are suggestive of a free radical chain mechanism rather than an ionic mechanism.

Further evidence for this pathway was obtained by using primary olefins as substrates. An ionic mechanism involving positive bromine would result in bromine in the terminal position, whereas a free radical chain mechanism with $\cdot NFCO_2R$ as the propagating species would give the reverse product. The latter was observed.

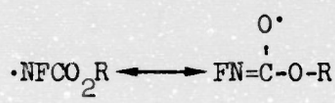
Thus, 1-hexene and isopropyl bromofluorocarbamate gave 1-(N-carboisopropoxyfluoramino)-2-bromohexane. Vinyl acetate and isopropyl chlorofluorocarbamate similarly gave α-chloro-β-(N-carboisopropoxyfluoramino)ethyl acetate. These compounds were identified by elemental analysis, and the direction of addition was unequivocally demonstrated by nmr spectra. Ethyl vinyl ether also gave 1:1 adducts with the bromofluoro and chlorofluorocarbamates, but the fluorine nmr spectra of both showed "doublets" at ϕ 47, J = 15.5 cps. The products do not appear to be the reverse adducts because the fluorine spectrum of $EtOCH(CH_3)NFCO_2Et$ is a doublet at ϕ 96.3, J = 33 cps.[1] The above "doublets" are interpreted as the center members of AB quartets in the structure, $R'O\overset{*}{C}HXCH_2NFCO_2R$.

Since the creation of a positive charge, but not of a free radical, adjacent to a carbonyl is very unfavorable,[3] acrylates can be used as diagnostic substrates for the mechanism of additions of nitrogen-halogen compounds to olefins.[4] Isopropyl bromofluorocarbamate reacted with ethyl acrylate and with methyl acrylate to give ethyl and methyl α-bromo-β-(N-carboisopropoxyfluoroamino)propionate, respectively. Traces of N-carboethoxy-N-fluoro-β-aminopropionates were also formed by hydrogen abstraction. The bromofluorocarbamate also reacted with methyl methacrylate to give methyl α-bromo-α-methyl-β(N-carboisopropoxyfluoroamino)propionate, with methyl crotonate to give methyl α-bromo-β-(N-carboisopropoxyfluoramino)butyrate, and with acrylonitrile to give α-bromo-β-(N-carboisopropoxyfluoramino)propionitrile, all in essentially quantitative yields.

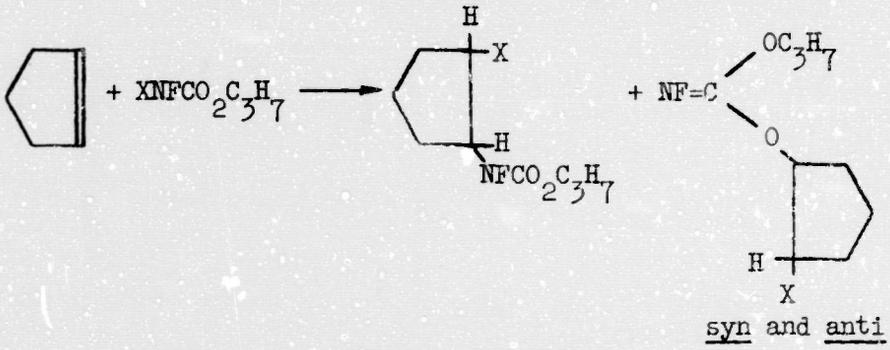
The direction of addition was consistent with a free radical chain mechanism in which the fluoraminocarboalkoxyl radical adds to the olefins to give the most stable adduct radical. The latter can then abstract bromine from the starting material to give the primary product. Side reactions involve hydrogen abstraction by the radical intermediates.



The fluoraminocarboalkoxy radical would be expected to be a resonating species with reactive sites at the nitrogen and the oxygen:

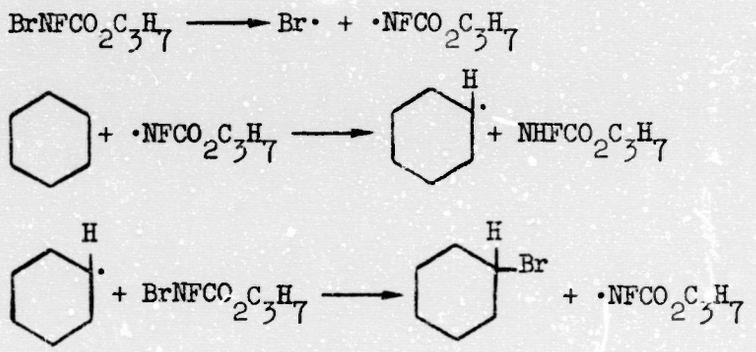


The addition of halofluorocarbamates to cyclopentene provided evidence for reaction at the oxygen site. The products of these reactions, employing either chlorofluorocarbamate or bromofluorocarbamate, analyzed for the expected isopropyl 2-halocyclopentylfluorocarbamates and the yields in both cases were practically quantitative. The fluorine nmr spectrum of the isopropyl chlorofluorocarbamate adduct consisted of a doublet at ϕ 88.4, J = 42.5 cps, and two weaker singlets of 84.6 and 87.0. The combined relative area of the singlets amounted to 5-10% of the total. The doublet is as expected for isopropyl 2-chlorocyclopentylfluorocarbamate, and the two singlets are assignable to the syn and anti isomers of 2-chlorocyclopentyl isopropyl fluoriminocarbonates. Syn and anti n-butyl methyl fluoriminocarbonates were reported by Stevens[5] to give signals at ϕ 89.6 and 90.0. The infrared spectra of the fluorocarbamate-cyclopentene products exhibited characteristic carbamate C=O absorption peaks at 5.70 and 5.81 μ, and also a relatively intense peak at 6.16 μ assigned to FN=C . Stevens' fluoriminocarbonates absorbed at 6.15-6.20 μ.[6]

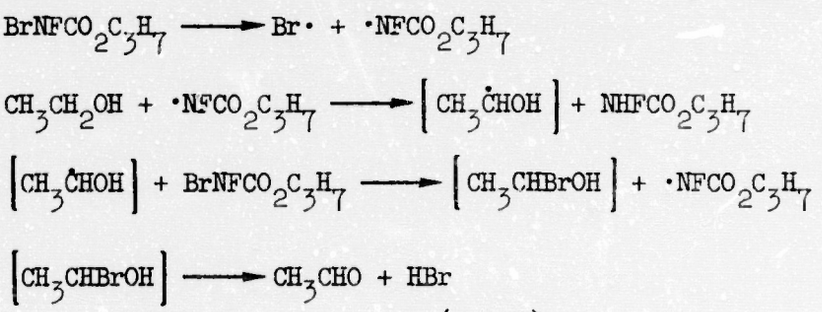


syn and anti

Isopropyl bromofluorocarbamate reacted with cyclohexane as a free radical brominating agent; bromocyclohexane and isopropyl fluorocarbamate were obtained in 92-93% yield. The following mechanism, which is analogous to that of the reaction of bromine with cyclohexane[7], is proposed.



Isopropyl chlorofluorocarbamate and bromofluorocarbamate reacted slowly with ethanol at ambient temperature. The bromofluorocarbamate reaction product was characterized as diisopropyl 2-bromoethylidinedicarbamate by elemental analysis and nmr spectra. The multi-step reaction apparently proceeded by the following free-radical mechanism:



(cont.)

$$NHFCO_2C_3H_7 + HBr \longrightarrow NH_2CO_2C_3H_7 + 1/2\ Br_2$$

$$CH_3CHO + Br_2 \longrightarrow BrCH_2CHO + HBr$$

$$BrCH_2CHO + 2NH_2CO_2C_3H_7 \xrightarrow{(H^+)} BrCH_2CH(NHCO_2C_3H_7)_2$$

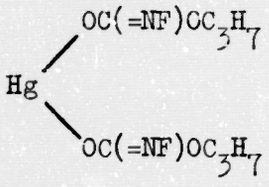
This mechanism involves bromination of ethanol and elimination of HBr to give acetaldehyde. Hydrogen bromide was shown in a separate test-tube experiment to reduce isopropyl fluorocarbamate to isopropyl carbamate, and the liberated bromine is consumed in the bromination of acetaldehyde to bromoacetaldehyde. The condensation between the aldehyde and two moles of the carbamate has been reported[8]. The analogous reaction of isopropyl chlorofluorocarbamate yielded isopropyl fluorocarbamate. In this case the reaction proceeded by the first four steps of the above proposed mechanism. Chloride, unlike bromide, is not oxidized by fluorocarbamates and therefore fluorocarbamate was the end product in this reaction.

The work on the reactions of mercury nitroform[9], and more recently the synthesis and reactions of bis(dinitrofluoromethyl)mercury[10] suggested that fluorocarbamates might give the analogous mercury derivatives. Accordingly, following the procedure employed in the synthesis of bis(fluorodinitromethyl)-mercury, moist mercuric oxide was reacted with two moles of isopropyl fluoro-carbamate to give a white micro-crystalline solid which was identified as bis(carboisopropoxyfluoramino)mercury:

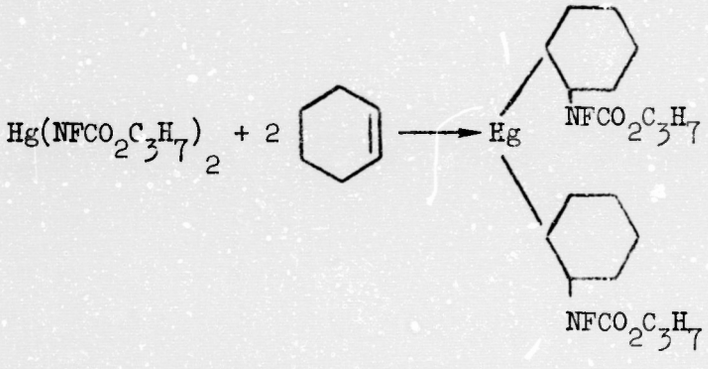
$$2\ NHFCO_2C_3H_7 + HgO \xrightarrow{Et_2O} Hg(NFCO_2C_3H_7)_2$$

The compound was characterized by elemental analysis and nmr spectra. The proton spectrum consisted of a septet and a doublet for the isopropyl group, and the fluorine spectrum exhibited a broadened signal at ϕ 88.9. The compound is soluble in organic solvents and stable at room temperature. It melts with decomposition of 136-7°. Its differential thermal analysis exhibited an endo-therm of 134°, followed by a sharp exhotherm (peak at 150°).[11]

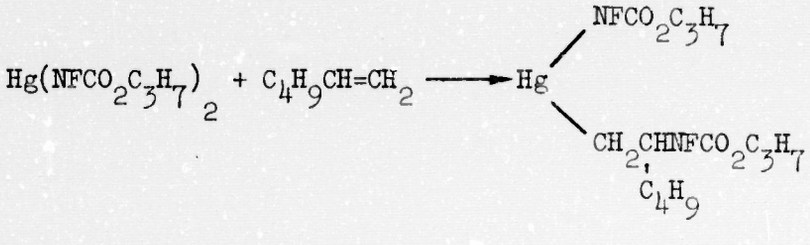
An isomeric structure involving mercury-oxygen bonding cannot be ruled out.



Bis(carboisopropoxyfluoramino)mercury represents the first reported metal-NF compound and a study of its reactions has been initiated. In a manner analogous to the reported reactions of bis(trinitromethyl)mercury[12], bis(carboisopropoxyfluoramino)mercury reacted with cyclohexene to give the insertion product:



The reaction was slow at 25° (4 days) and the product was only moderately stable at room temperature. Bis(carboisopropoxyfluoramino)mercury reacted more slowly with hexene-1. The reaction required 8 days and gave the 1:1 insertion product, carboisopropoxyfluoramino-2(carboisopropoxyfluoramino)hexylmercury:



The compound was characterized by elemental analysis. Its fluorine nmr spectrum consisted of two symmetrically superimposed signals at ϕ 97.2: a doublet, J_{HF} = 37.5 cps, and a 1:1:1 triplet, J_{NF} = 243 cps, assigned to – CHNF – and

– HgNF – fluorines, respectively. The J_{HF} of the doublet is typical for –C–N–F– configuration eliminating the possibility of –OC(=NF)O– bonding. The N-F coupling of the –HgNF– fluorine seems to be consistent with the observed very broad signal of bis(carboisopropoxyfluoramino)mercury, which, too, might resolve into a 1:1:1 triplet at a lower temperature.

The above reactions of bis(carboisopropoxyfluoramino)mercury indicate broad utility in the synthesis of NF compounds.

Experimental

Isopropyl N-Chloro-N-fluorocarbamate. - To a stirred solution of 4.0 g (0.1 mol) of sodium hydroxide in 100 ml of ice-water at 0° was added 12.1 g (0.1 mol) of isopropyl N-fluorocarbamate and the resulting solution was chlorinated at 0-3° (15 min) with gaseous chlorine until the mixture became slightly acidic (pH 5-6). The water-insoluble liquid was extracted with 75 ml of methylene chloride and the extract was distilled to give 10.2 g (66% yield) of isopropyl N-chloro-N-fluorocarbamate, bp 42°/25 mm.

Anal. Calcd for $C_4H_7NFClO_2$: C, 30.9; H, 4.5; N, 9.0; F, 12.2. Found: C, 30.7; H, 4.3; N, 8.6; F, 11.8.

The proton nmr spectrum in carbon tetrachloride exhibited a septet at δ 5.11, J = 6.2 cps, and a doublet at 1.41, J = 6.2 cps. The fluorine spectrum consisted of a broadened singlet at ϕ -2.56.

Further distillation gave 1.7 g of diisopropyl N-fluoriminodicarboxylate (16.4% yield), bp 68-69°/0.2 mm (reported[13] bp 68°/0.2 mm).

Isopropyl N-Bromo-N-fluorocarbamate. - The above procedure using 16.0 g (0.1 mol) of bromine instead of chlorine, gave 15.1 g (76% yield) of isopropyl N-bromo-N-fluorocarbamate, an orange-red liquid, bp 27°/0.05 mm, n_D^{25} 1.4365.

Anal. Calcd for $C_4H_7NFBrO_2$: C, 24.0; H, 3.5; N, 7.0; F, 9.5. Found: C, 24.2; H, 3.5; N, 6.7; F, 8.9.

The proton nmr spectrum in carbon tetrachloride showed a septet at δ 5.09, J = 6.2 cps and a doublet at 1.41, J = 6.2 cps. The fluorine spectrum exhibited a broadened singlet at ϕ 5.52.

Isopropyl N,N-Dibromocarbamate. - To a stirred cold (0-2°) solution of 4.0 g (0.1 mol) of sodium hydroxide and 5.15 g (0.05 mol) of isopropyl carbamate was added dropwise with cooling 16.0 g (0.1 mol) of bromine (10 min). A bright-yellow solid was filtered and washed with three 30 ml portions of ice-water. Crystallization from carbon tetrachloride gave 6.5 g of isopropyl N,N-dibromocarbamate, mp 66-67° (50% yield).

Anal. Calcd for $C_4H_7NBr_2O_2$: C, 18.4; H, 2.7; N, 5.4. Found: C, 18.3; H, 2.5; N, 5.1.

The proton nmr spectrum in $CDCl_3$-carbon tetrachloride mixture consisted of a septet at δ 4.92, J = 6.2 cps; and a doublet at 1.34, J = 6.2 cps.

1-Bromo-2-(N-carboisopropoxyfluoramino)cyclohexane. - To 4.0 g (0.05 mol) of cyclohexene was added at 25° 1.0 g (0.005 mol) of isopropyl bromofluorocarbamate. In 20-30 sec, the orange-yellow reaction mixture heated to 60-65° and turned colorless. After a few minutes the exothermic reaction subsided, and after 15 min the solution was distilled to give 1.35 g (95% yield) of 1-bromo-2-(N-carboisopropoxyfluoramino)cyclohexane, colorless liquid, bp 93-94°/0.025 mm.

Anal. Calcd for $C_{10}H_{17}NFBrO_2$: C, 42.6; H, 6.0; N, 5.0; F, 6.7. Found: C, 42.8; H, 6.0; N, 4.7; F, 6.5.

The proton nmr spectrum in carbon tetrachloride consisted of a septet at δ 4.90, J = 6.1 cps, for $-\underline{CH}(CH_3)_2$, a complex superposition of multiplets centered at 256 cps representing two methine protons of the cyclohexane ring, a superposition of multiplets centered at 110 cps for methylene groups, and a doublet at δ 1.43, J = 6.1 cps, for the two methyl groups. The fluorine spectrum exhibited three doublets at ϕ 86.1, J = 29.5 cps, ϕ 93.8, J = 36.8 cps, and ϕ 87.5, J = 31.2 cps with approximate relative area ratio of 0.9:1.0:0.1.

1-Chloro-2-(N-carboisopropoxyfluoramino)cyclohexane. - Following the above procedure, the reaction of isopropyl chlorofluorocarbamate, 1.1 g (0.007 mol), with cyclohexene (4.0 g) gave 1.45 g (86% yield) of 1-chloro-2-(N-carboisopropoxyfluoramino)cyclohexane, bp 81-82°/0.025 mm, n_D^{25} 1.4600. The reaction required 6-7 hours for completion.

Anal. Calcd for $C_{10}H_{17}NFClO_2$: C, 50.5; H, 7.2; N, 5.9; F, 8.0. Found: C, 50.3; H, 7.3; N, 5.5; F, 7.7.

The proton nmr spectrum in carbon tetrachloride consisted of a septet of δ 5.00, J = 6.2 cps, for –CH– of the isopropyl group, a complex superposition at multiplets centered at 250 cps for the two cyclohexyl methine protons, a

complex multiplet at 110 cps for the four CH_2 groups of the cyclohexane ring, and a superimposed doublet at 1.32, J = 6.2 cps, for the isopropyl methyl groups. The fluorine spectrum exhibited three doublets at ϕ 85.7, J = 30.3 cps, ϕ 94.1, J = 36.6 cps, and ϕ 87.5, with approximate relative areas of 3:10:0.5. The first two doublets were assigned to cis and trans adducts. The weak doublet at ϕ 87.5 was assigned to isopropyl cyclohexylfluorocarbamate.

The fluorine nmr spectrum of ethyl N-cyclohexyl-N-fluorocarbamate[1] exhibited a doublet at ϕ 92.1, J_{HF} = 37.2 cps.

1-(N-Carboisopropoxyfluoramino)-2-bromohexane. - Isopropyl bromofluorocarbamate, 1.0 g (0.005 mol) was added to 4.0 g (0.047 mol) of hexene-1. No visible reaction. The solution was warmed at 45-48° for 45 min, during which time the orange-yellow color of the carbamate was completely "bleached." The reaction mixture was distilled to give 1.35 g (95% yield) of 1-(N-carboisopropoxyfluoramino)-2-bromohexane, colorless liquid, bp 72°/0.025 mm.

Anal. Calcd for $C_{10}H_{19}NFBrO_2$: C, 42.3; H, 6.7; N, 4.9; F, 6.7. Found: C, 42.0; H, 6.7; N, 4.8; F, 6.9.

The proton nmr spectrum in carbon tetrachloride consisted of a septet at δ 5.01, J = 6.2 cps, for $-CH(CH_3)_2$, superimposed multiplets at 256 cps for -CHBr- and one proton of $-CH_2-$ adjacent to the asymmetric carbon, the other leg of the AB pattern at 227 cps for the other proton of the $-CH_2-$ group adjacent to the asymmetric carbon, a complex superposition of patterns between 125 and 80 cps for the remaining CH_2 groups, a doublet at 1.33, J = 6.2 cps, for $-CH(CH_3)_2$, and a distorted triplet at 0.93 for CH_3. The fluorine spectrum exhibited a distorted triplet at ϕ 65.9, J_{HF} = 33.0 cps. A minute doublet at ϕ 96.3, J_{HF} = 36.5 cps, was attributed to a small amount of isopropyl n-hexylfluorocarbamate.

Isopropyl N-Fluoro-N-(2-bromo-2-ethoxy)ethylcarbamate. - To a stirred solution of 0.8 g (0.011 mol) of ethyl vinyl ether in 30 ml of methylene chloride was added dropwise at 25° over a period of 3 min 2.0 g (0.01 mol) of isopropyl bromofluorocarbamate. The orange-red color of the carbamate was discharged instantaneously and the reaction temperature increased to 38-39° at

the end of the addition. After a few minutes, the reaction mixture was distilled to give 2.7 g (100% yield) of isopropyl N-fluoro-N-(2-bromo-2-ethoxy)-ethylcarbamate, bp 67-68°/0.05 mm, n_D^{22} 1.4450.

Anal. Calcd for $C_8H_{15}NFBrO_3$: C, 35.3; H, 5.5; N, 5.2; F, 7.0. Found: C, 35.1; H, 5.6; N, 5.3; F, 7.1.

The infrared spectrum consisted of the following peaks (μ): 3.37(m); 3.41(m); 3.46(sh); 5.68(s); 5.81(s); 6.11(vw); 6.84(m); 6.90(m); 7.02(m); 7.15(sh); 7.22(SH); 7.30(s); 7.71(s); 7.85(sh); 8.12(m); 8.44(m); 8.65(sh); 9.08(s); 9.45(s); 11.02(s); 11.95(m); 13.15(w); 14.55(w); and 14.95(w).

The proton nmr spectrum in carbon tetrachloride consisted of a multiplet (AB pattern ?) at δ5.6, superposition of $-\underline{CH}(CH_3)_2$ on other multiplets at 5.1, superposition of two quartets of $-O\underline{CH_2}CH_3$ at 3.7, a multiplet at 3.6, a doublet at 1.35, J = 6.2 cps, for $-CH(\underline{CH_3})_2$, and a triplet at 1.21, J = 7.3 cps, for $-CH(\underline{CH_3})_2$. The fluorine spectrum exhibited a doublet at ∅ 47.0, J_{HF} = 15.5 cps, and a minute doublet at 58.6, J_{HF} = 35 cps.

Isopropyl N-Fluoro-N-(2-Chloro-2-ethoxy)ethylcarbamate. - The reaction of isopropyl chlorofluorocarbamate, 1.56 g (0.01 mol), with 0.72 g (0.01 mol) of ethyl vinyl ether, following the above procedure, gave 2.0 g (88% yield) of isopropyl N-fluoro-N-(2-chloro-2-ethoxy)ethylcarbamate, colorless liquid, bp 57-58°/0.05 mm, n_D^{22} 1.4265.

Anal. Calcd for $C_8H_{15}NFClO_3$: C, 42.2; H, 6.6; N, 6.2; F, 8.4. Found: C, 42.0; H, 6.7; N, 6.1; F, 8.3.

The proton nmr spectrum in carbon tetrachloride consisted of a multiplet at δ5.6 (AB pattern ?), a septet at 5.07, J = 6.2 cps, for $-\underline{CH}(CH_3)_2$ superimposed on another multiplet, a double quartet at 3.7 for $-O\underline{CH_2}CH_3$, a distorted "doublet" (?) at 3.7, a doublet at 1.35, J = 6.2 cps, for $-CH(\underline{CH_3})_2$, and a triplet at 1.22, J = 7.3 cps, for $-OCH_2\underline{CH_3}$. The fluorine spectrum exhibited a doublet of ∅ 47.3, J_{HF} = 15.8 cps, and five other very weak signals attributed to trace-amounts of side-reaction products: two X portions of ABX patterns at ∅ 34.3 and 35.2, a singlet at 4.16, a doublet, J ≅ 20 cps at 45.8, and a doublet, J ≅ 30 cps at 58.7.

1-Chloro-2-(N-carboisopropoxy-N-fluoramino)ethyl Acetate. - A solution of 0.86 g (0.01 mol) of vinyl acetate and 1.56 g (0.01 mol) of isopropyl chlorofluorocarbamate in 20 ml of methylene chloride was allowed to stand at 25° for 4 days. Hydroquinone, the polymerization inhibitor in the acetate was not removed and air was not excluded. The reaction mixture was distilled to give 1.0 g of unreacted isopropyl chlorofluorocarbamate, bp 42°/25 mm (64% recovery) and 0.65 g (77% yield) of 1-chloro-2-(N-carboisopropoxy-N-fluoramino)-ethyl acetate, bp 77°/0.05 mm.

Anal. Calcd for $C_8H_{13}NFClO_3$: C, 39.6; H, 5.4; N, 5.8; F, 7.8. Found: C, 39.7; H, 5.6; N, 6.0; F, 8.0.

The fluorine nmr spectrum in carbon tetrachloride exhibited a six-line pattern at ϕ 66.9, the X portion of ABX quartet with the separation of outer wings from the center by 30.6 cps and inner (almost superimposed) wings by 1.5 cps. A weak doublet at ϕ 116.3, J = 55 cps, was exhibited by a trace-amount of isopropyl fluorocarbamate.

Ethyl α-Bromo-β-(N-carboisopropoxyfluoramino)propionate. - A solution of 1.0 g (0.01 mol) of ethyl acrylate* and 1.15 g (0.0058 mol) of isopropyl bromofluorocarbamate 15 ml of methylene chloride was allowed to stand at room temperature (air and light not excluded) for 8 days, until the orange-red color of the carbamate was completely "bleached." The mixture was distilled to give 0.95 g of ethyl α-bromo-β-(N-carboisopropoxyfluoramino)propionate, bp 95-96°/0.05 mm, n_D^{22} 1.4435.

Anal. Calcd for $C_9H_{15}NFBrO_4$: C, 36.0; H, 5.0; N, 4.7; F, 6.3. Found: C, 36.3; H, 5.1; N, 4.9; F, 6.6.

The proton nmr spectrum in carbon tetrachloride consisted of a septet at δ 5.02, J = 6.3 cps, for $-\underline{CH}(CH_3)_2$, complex multiplets at 5.0 and 4.5, a quartet at 4.25, J = 7.2 cps, for $-O\underline{CH_2}CH_3$, a triplet at 1.30 for $-OCH_2\underline{CH_3}$, and a doublet at 1.34 for $-CH(\underline{CH_3})_2$. The fluorine spectrum exhibited a complex three-membered multiplet at ϕ 66.8 cps, with outer wings ∿31 cps from the center.

*Stabilized with 0.02% of MEHQ.

Other three very weak signals, a triplet at ϕ 62.7, J = 32.0 cps, a triplet at 73.4, J = 29.2 cps, and a doublet at 82.7, J = 36.7 cps, were also present in the spectrum.

Methyl α-Bromo-β-(N-carboisopropoxyfluoramino)propionate. - The above procedure using 0.96 g (0.011 mol) of freshly distilled methyl acrylate and 2.0 g (0.01 mol) of isopropyl N-bromo-N-fluorocarbamate gave 1.6 g of methyl α-bromo-β-(N-carboisopropoxyfluoramino)propionate, colorless liquid, bp 83°/ 0.1 mm.

Anal. Calcd for $C_8H_{13}NFBrO_4$: C, 33.6; H, 4.6; N, 4.9; F, 6.6. Found: C, 33.4; H, 4.6; N, 5.2; F, 6.6.

The proton nmr spectrum in carbon tetrachloride consisted of a septet at δ 5.03, J = 6.2 cps, for $-\underline{CH}(CH_3)_2$, a complex AB pattern at 4.8 superimposed on the above signal, a multiplet at 4.8 for –CHBr– (superimposed), a singlet at 3.82 for OCH_3 (superimposed on an unidentified multiplet), and a doublet at 1.35 for $-CH(CH_3)_2$. The fluorine spectrum consisted of a complex three-legged multiplet at $\overline{\phi}$ 67.1, with outer wings at ∿31 cps from the center. As it was the case with ethyl acrylate product, the material contained small amounts of contaminants exhibiting weal signals at ϕ 62.9 (triplet, J = 30.2 cps), 73.0 (triplet, J $\cong$ 30 cps), and 83.1 (doublet, J $\cong$ 35 cps).

Methyl α-Bromo-α-methyl-β-(N-carboisopropoxyfluoramino)propionate. - A solution of 1.0 g (0.01 mol) of methyl methacrylate and 2.0 g (0.01 mol) of isopropyl bromofluorocarbamate in 15 ml of methylene chloride was allowed to stand at 25° until the orange-yellow color of the carbamate was "bleached" (18 hrs). The reaction mixture was not protected from light and air. The solution was distilled to give 2.95 g (98% yield) of methyl α-bromo-α-methyl-β-(N-carboisopropoxyfluoramino)propionate, colorless liquid, bp 79-80°/0.05 mm, n_D^{22} 1.4530.

Anal. Calcd for $C_9H_{15}NFBrO_4$: C, 36.0; H, 5.0; N, 4.7; F, 6.3. Found: C, 35.7; H, 5.1; N, 4.8; F, 6.4.

The proton nmr spectrum in carbon tetrachloride consisted of a septet at δ 5.03, J = 6.0 cps, for $-\underline{C}H(CH_3)_2$ protons, a low-field AB portion of ABX pattern at 4.62 and high-field AB portion of the same pattern at 4.05 for the methylene group, a singlet at 3.81 for $-OCH_3$, a broadened singlet at 1.96 for the methyl group, and a doublet, J = 6.0 cps, at 1.34 for $-CH(C\underline{H}_3)$. The fluorine spectrum consisted of a four-line signal, the X portion of ABX pattern at ϕ 58.9. (Outer members separated by 2.6 cps; spacing between center and outer members = 32.9 cps.)

Methyl α-Bromo-β-(N-carboisopropoxyfluoramino)butyrate. - Following the above procedure, methyl crotonate, 0.5 g (0.005 mol), and isopropyl bromofluorocarbamate, 1.0 g (0.005 mol) gave (84 hrs at 25°) 1.4 g (93% yield) of methyl α-bromo-β-(N-carboisopropoxyfluoramino)butyrate, colorless liquid, bp 81-82°/0.05 mm.

Anal. Calcd for $C_9H_{15}NFBrO_3$: C, 36.0; H, 5.0; N, 4.7; F, 6.3. Found: C, 35.7; H, 5.0; N, 4.5; F, 6.3.

The proton nmr spectrum in carbon tetrachloride consisted of a septet at ∿δ 5.04, J = 6.3 cps, for $-\underline{C}H(CH_3)_2$, a multiplet centered at 4.6 for –CHF– [partially superimposed over $-CH(C\underline{H}_3)_2$ and –CHBr–], a doublet at 4.4 for –CHBr– (superimposed on $-CH_2-$ quartet), two very closely spaced singlets at 3.8 for $-OCH_3$, and doublets of the three methyl groups at 1.36. The fluorine spectrum exhibited two doublets at ϕ 44.8, J_{HF} = 19 cps, and 46.3, J_{HF} = 20.6 cps, of approximate relative area ratio of 1:3, respectively, assigned to two enantiomorphs of the compound.

α-Bromo-β-(N-carboisopropoxyfluoramino)propionitrile. - A solution of 0.3 g (0.0057 mol) of acrylonitrile and 1.0 g (0.005 mol) of isopropyl bromofluorocarbamate in 8 ml of methylene chloride was allowed to stand at 25° for 16 hrs. The colorless solution was distilled to give 1.2 g (95% yield) of α-bromo-β-(N-carboisopropoxyfluoramino)propionitrile, bp 81°/0.05 mm, n_D^{22} 1.4610.

Anal. Calcd for $C_7H_{10}N_2FBrO_2$: C, 33.2; H, 4.0; N, 11.1; F, 7.5. Found: C, 32.8; H, 3.8; N, 10.7; F, 7.6.

The proton nmr spectrum in carbon tetrachloride consisted of a septet at δ 5.06, J_{HH} = 6.1 cps, for the methine proton of the isopropyl group, the low-field AB portion (scewed doublet, J = 6.7 cps) of ABX pattern at 4.7 for –CHBr–, the high-field AB portion of the same pattern at 4.00, and a doublet at 1.37 for $-CH(C\underline{H}_3)_2$, J_{HH} = 6.1 cps. The fluorine spectrum exhibited a signal at ϕ 65.5, a three-legged X portion of ABX pattern with center members superimposed and outer members separated from the center by 30.6 cps.

Reaction of Isopropyl Bromofluorocarbamate with Cyclopentene. - To a solution of 0.4 g (0.0051 mol) of cyclopentene in 25 ml of methylene chloride at 25° was added 1.0 g (0.005 mol) of isopropyl bromofluorocarbamate. In a few seconds the reaction mixture began to warm and was cooled to keep its temperature at 25° - 30°. In ca 10 min the orange-yellow reaction mixture turned colorless and was distilled to give 1.25 g of colorless liquid, bp 75-77°/ 0.05 mm; no distillation residue.

Anal. Calcd for $C_9H_{15}NBrFO_2$: C, 40.3; H, 5.6; N, 5.2; F, 7.1. Found: C, 40.0; H, 5.3; N, 5.0; F, 7.3.

The proton nmr spectrum in carbon tetrachloride consisted of a septet at δ 5.02, J = 6.2 cps, for $-C\underline{H}(CH_3)_2$, a multiplet centered at 4.6 [partially superimposed by –CHBr– and $-C\underline{H}(CH_3)_2$ signals] for –CHNF–, a multiplet at 4.3 for –CHBr–, a multiplet at 1.91 for the three $-CH_2-$ groups, and a doublet at 1.34, J = 6.2 cps, for $-CH(C\underline{H}_3)_2$. The fluorine spectrum exhibited a doublet at ϕ 88.8, J_{HF} = 43.4 cps. Two singlets at ϕ 84.7 and 87.0, with combined area amounting to ca 15% of the doublet, were assigned to syn and anti isomers of 2-bromocyclohexyl isopropyl fluoriminocarbonate.

Reaction of Isopropyl Chlorofluorocarbamate with Cyclopentene. - Following the above procedure, isopropyl chlorofluorocarbamate, 3.1 g (0.02 mol), was reacted with cyclopentene, 1.5 g (0.022 mol) in 20 ml of methylene chloride. The reaction was slow and required 3 to 4 days for completion. The mixture was distilled to give 3.9 g of colorless liquid, bp 65-67°/0.05 mm.

Anal. Calcd for $C_9H_{15}NFClO_2$: C, 48.3; H, 6.7; N, 6.3; F, 8.5. Found: C, 47.9; H, 6.6; N, 6.3; F, 8.3.

The infrared spectrum consisted of the following peaks (μ): 3.38(s); 3.49(w); 5.70(s); 5.84(s); 6.17(m); 6.85(m); 6.91(w); 7.20(sh); 7.22(m); 7.29(s); 7.60-7.90(s; broad); 8.46(m); 8.73(m); 9.05(s); 9.32(m); 9.70(m); 9.90(sh); 10.50(sh); 10.15-10.30(w; broad); 11.04(w); 12.0(m) and 12.90(w).

The proton nmr spectrum in carbon tetrachloride consisted of a septet at δ 5.03, J = 6.2 cps, for $-\underline{CH}(CH_3)_2$, a multiplet at ca 4.6 for -CHNF-, a multiplet at 4.3 for -CHCl-, a multiplet at 1.9 for the three methylene groups of cyclopentane ring, and a doublet at 1.32, J = 6.1 cps, for $-CH(\underline{CH_3})_2$. The spectrum also exhibited another weak doublet at 1.34. The fluorine spectrum showed a doublet at ϕ 88.4, J_{HF} = 42.5 cps. Two weak singlets at ϕ 84.6 and 87.0, were assigned to syn and anti isomers at 2-chlorocyclopentyl isopropyl fluoriminocarbonate. The relative combined area of these two signals amounted to ca 5-10% of the ϕ 88.4 signal.

Reaction of Isopropyl N-Bromo-N-fluorocarbamate with Cyclohexane. - A solution of 2.7 g (0.0135 mol) of isopropyl bromofluorocarbamate in 35 ml of cyclohexane (spectro grade) was allowed to stand at 25° for 18 hrs during which time the orange-yellow solution turned colorless. The reaction mixture was not protected from air and light. The solution was distilled to give 2.05 g of bromocyclohexane, bp 57-58°/20 mm (93% yield), identified by its infrared spectrum,[14] and 1.5 g of isopropyl N-fluorocarbamate (92% yield), bp 29-30°, also identified by infrared spectrum.[1]

Reaction if Isopropyl N-Bromo-N-fluorocarbamate with Ethanol. - Isopropyl N-bromo-N-fluorocarbamate, 5.0 g (0.025 mol), was added to 45 ml of absolute ethanol at 25°. A mildly exothermic reaction took place and the reaction mixture warmed by itself to 35° in 10 min. At the same time, the color of the solution intensified from pale-yellow to deep orange-red. The reaction mixture was cooled to 25° and allowed to stand at this temperature until it became colorless (6 days). The solution was evaporated to dryness to leave 3.8 g of a white solid. The material was recrystallized from methanol-water mixture to give 3.5 g of diisopropyl bromoethylidinedicarbamate, mp 166-167°.

Anal. Calcd for $C_{10}H_{19}N_2BrO_4$: C, 38.6; H, 6.1; N, 9.0. Found: C, 38.4; H, 6.1; N, 9.0.

The proton nmr spectrum in d_6-acetone consisted of a broadened singlet at δ 6.6 for the —NH— protons, an irregular quintet at 5.39 for $BrCH_2\underline{CH}$—, a septet at 4.87, J = 6.3 cps, for the two methine protons of the isopropyl groups, a doublet at 3.68, J = 6.8 cps, for $Br\underline{CH}_2$, and a doublet at 1.22, J = 6.3 cps, for the four methyl groups.

Reaction Between Isopropyl Chlorofluorocarbamate and Ethanol. - To 35 ml of absolute ethanol at 25° was added 3.5 g (0.0225 mol) of isopropyl chlorofluorocarbamate. After 7-8 min the reaction mixture began to warm and heated by itself to 75-80° in a matter of a few minutes. The exothermic reaction was over in 5-8 min. The reaction mixture was distilled to give 2.2 g of isopropyl N-fluorocarbamate, bp 30°/0.1 mm (81% yield) identified by comparing its proton nmr spectrum with that of authentic material.

Bis(N-Carboisopropoxy-N-fluoramino)mercury. - To a solution of 6.1 g (0.05 mol) of isopropyl fluorocarbamate in 170 ml of moist ether (170 ml of anhydrous ether + 1 ml of water) was added 5.0 g (0.023 mol) of yellow mercuric oxide (powder) and the mixture was stirred at 25°. After a few hours, the reaction mixture began to deposit some white solid, and the orange-red color of the mixture was gradually "bleached." After 16 hrs, the reaction mixture was filtered and the orange-red filter cake was washed with 50 ml of diethyl ether. The combined filtrate and washings were evaporated to dryness to give 3.5 g of white solid which was crystallized from chloroform to give 2.9 g of bis(N-carboisopropoxy-N-fluoramino)mercury, mp 136-7°(d). The differential thermal analysis showed an endotherm at 134° followed by a sharp exotherm.

Anal. Calcd for $C_8H_{14}N_2F_2O_4Hg$: C, 21.8; H, 3.2; N, 6.4; F, 8.6. Found: C, 21.6; H, 3.0; N, 6.4; F, 8.7.

The proton nmr spectrum in $CDCl_3$ consisted of a septet at δ 5.08, J = 6.2 cps for —CH—, and a doublet at 1.34 for the methyl protons. The fluorine spectrum exhibited a very broad singlet at ϕ 88.9.

The filter cake above contained mainly the bis-mercury compound contaminated with a small amount of unreacted mercuric oxide. The crude material was treated with boiling chloroform and filtered to remove 0.7 g of H_gO. Bis(N-carboisopropoxy-N-fluoramino)mercury, 5.0 g, crystallized from the filtrate.

In another identical experiment, the reaction mixture was evaporated to dryness at reduced pressure and the crude solid was crystallized from chloroform to give the mercury compound in 91% yield.

Bis 2-(Carboisopropoxyfluoramino)cyclohexylmercury. - A suspension of 0.5 g (0.00114 mol) of bis(N-carboisopropoxy-N-fluoramino)mercury in 3.8 g of cyclohexene was allowed to stand at 25°. No visible reaction occurred for several days, but a clear solution resulted after 4 days. No further changes were noticed during the next several days. The reaction mixture was concentrated to remove the excess of cyclohexene to leave 0.7 g of bis 2-(carboisopropoxyfluoramino)cyclohexylmercury, colorless liquid, n_D^{25} = 1.4970, which was not further purified.

Anal. Calcd for $C_{20}H_{34}N_2F_2O_4Hg$: C, 39.7; H, 5.6; N, 4.6; F, 6.3. Found: C, 40.1; H, 5.5; N, 3.9; F, 5.5.

N-Carboisopropoxyfluoramino-2-(carboisopropoxyfluoramino)hexylmercury. - A suspension of 0.8 g of bis(N-carboisopropoxyfluoramino)mercury in 15 ml of hexene-1 was allowed to stand at 25° for 8 days. No visible changes occurred during the first 4-5 days. On the 6th day, it was noticed that ca 50% of the mercury compound was dissolved, and at the end of the 8th day a clear and colorless solution resulted. The solution was concentrated to remove unreacted hexene-1, and N-carboisopropoxyfluoramino-2-(N-carboisopropoxyfluoramino)-hexylmercury was dried at 45-50°/0.05 mm. The compound 0.95 g, was not further purified.

Anal. Calcd for $C_{14}H_{26}N_2F_2O_4Hg$: C, 32.1; H, 5.0; N, 5.3; F, 7.2. Found: C, 33.0; H, 5.3; N, 5.1; F, .

The fluorine nmr spectrum in carbon tetrachloride consisted of two superimposed signals at ∅ 97.2: a triplet, J_{N-F} = 243 cps, and a doublet, J_{HF} = 37.5 cps, assigned to —Hg-NF— and —CHNF— fluorines, respectively.

REFERENCES

1. Aerojet-General Report No. 0235-01-11, July 1961, p. 12 (Confidential); V. Grakauskas and K. Baum, J. Am. Chem. Soc., 91, 2679 (1969).

2. K. Schrange, Tetrahedron Letters, 46, 5795 (1966).

3. H. Schechter and F. Conrad, J. Amer. Chem. Soc., 75, 5610 (1953).

4. A. Hassner, J. E. Kropp, and G. J. Kent, J. Org. Chem., 34, 2629 (1969).

5. T. E. Stevens, J. Org. Chem., 33, 2660 (1968).

6. T. E. Stevens, Rohm and Haas Co., Private communication.

7. M. S. Kharasch, W. Hered, and F. R. Mayo, J. Org. Chem., 6, 818 (1941).

8. W. M. Kraft and R. M. Herbst, J. Org. Chem., 10, 483 (1945).

9. For review, see P. Noble, Jr., F. G. Borgardt, and W. L. White, Chem. Rev., 64, 20 (1964).

10. L. V. Obhlobystina, G. Ya. Legin and A. A. Fainzilberg, Izv. Ahad. Nauk SSSR, Ser. Khim, 1969, 708.

11. Earlier attempts to synthesize the above mercury compound by reacting isopropyl chlorofluorocarbamate with mercury [see Aerojet-General Technical Report AFRPL-TR-66-352, Contract AF04(612)-11215, December 1966] gave a solid, mp 105 108° with physical properties different from those of the mercury compound above. This material was only partially characterized.

12. V. A. Tartovkovski, L. A. Nikonova, and S. S. Novikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1966, 1290.

13. K. Baum, J. Org. Chem., 33, 4333 (1968).

14. "The Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Vol. 2, No. 2263.

APPENDIX A

Direct Fluorination of Ureas[1]

Vytautas Grakauskas and Kurt Baum

Contribution of the Environmental Systems Division
Aerojet-General Corporation, Azusa, California

ABSTRACT

Fluorourea and N, N-difluorourea were prepared by the direct fluorination of aqueous solutions or acetonitrile suspensions of urea. Fluorourea decomposed in aqueous solution to give azodicarbondiamide, and in the presence of urea, biurea. Fluorourea reacted with sulfuric acid to give fluorammonium ion, ammonium sulfite or hydrazine sulfate, depending on reaction conditions. Properties of N, N-difluorourea are described. The fluorination of alkylureas gave difluoraminoalkanes and N-alkyl-N', N'-difluoroureas, showing that the second fluorination step takes place at the same nitrogen as the first, whether a hydrogen or an acyl group is displaced. The fluorination of cyclic N, N'-disubstituted ureas gave ω-(difluoramino)isocyanates and carbamyl fluorides.

The fluorination of solid urea was reported by Glemser and Lüdemann[2] to give biurea and HF. along with some NH_3, COF_2, CO_2 and biuret. Although no NF compounds were identified, fluorourea was postulated to be an intermediate. Subsequently, Lawton, et al.[3,4] identified N, N-difluorourea as one of the products of fluorination under similar conditions, as well as CF_4, $(CF_3)_2NF$, $(CF_3)_3N$, HNF_2, and HCN. Less than a mole of fluorine per mole of urea was used.

The fluorination of aqueous solutions of urea was found in the present work[5] to be a more readily controllable reaction to produce N, N-difluorourea. This solution fluorination technique has also been applied to carbamates,[6,7] amides[8] and nitronate salts.[9] The moderating effect of the solvent allowed the use of two moles of fluorine, and a 74% yield of N, N-difluorourea was isolated by ether extraction. N, N-Difluorourea was also prepared by the fluorination of a suspension of urea in acetonitrile.

N, N-Difluorourea must be handled with caution, as it is a sensitive explosive and is toxic, but it is not changed on prolonged storage at room temperature. A sample was recovered almost quantitatively after 5 hrs in toluene at 110°. The compound is a white solid, mp 41-41.5° which was isolated in two crystalline forms, platelets by sublimation and needles by crystallization from halogenated solvents. The platelet form is hygroscopic whereas the needle form is not affected by atmospheric moisture. The amino group of N, N-difluorourea is unreactive, and further fluorination did not yield more highly fluorinated ureas.[10] No reaction took place in

5 hrs between difluorourea and bromine in carbon tetrachloride at 60°.

The crude aqueous fluorination product containing N, N-difluorourea (approximately 1M) and the byproduct, HF, can be stored for about one week at 0° without noticeable decomposition, and for several months frozen at -20°. This solution is hydrolyzed rapidly at 60-90° in the presence of sulfuric acid, and this reagent has become a widely used source of difluoramine.[5, 11-15] The reaction of the crude N, N-difluorourea solution with base has also been reported to be a convenient synthesis method for difluorodiazine.[15]

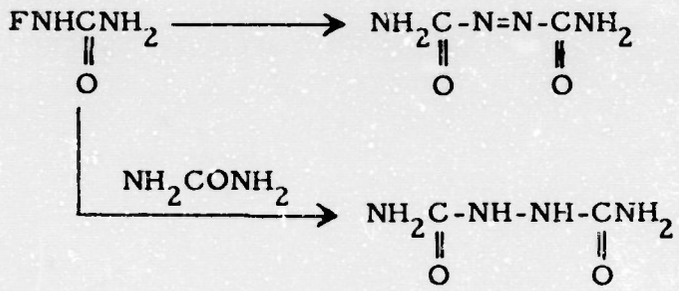
The expected intermediate in the formation of N, N-difluorourea, fluorourea, has not been isolated previously. With this objective an equimolar amount of fluorine was passed into an aqueous urea solution. Even under these conditions, the major product was N, N-difluorourea, but a 20% yield of fluorourea was isolated by extraction with ether and recrystallization from methylene chloride. Florourea is thus fluorinated more rapidly than urea in aqueous solutions. Acetonitrile was also used as a fluorination solvent, with the advantages of allowing lower reaction temperatures and more convenient product isolation. The fluorination of a suspension of urea in acetonitrile, using 0.6 mol of fluorine, thus gave a 53% yield of fluorourea based on fluorine.

$$NH_2\underset{\underset{O}{\|}}{C}NH_2 + F_2 \longrightarrow NH_2\underset{\underset{O}{\|}}{C}NHF + HF \xrightarrow{F_2} NH_2\underset{\underset{O}{\|}}{C}NF_2$$

Fluorourea is a white solid, mp 56-57°. The proton nmr spectrum in

tetrahydrofuran consists of broad signals at δ6.67 and 10.66 (area ratio 2:1) and the fluorine signal (+34.22 from trifluoroacetic acid) also shows no resolution. The lack of observable H-F coupling indicates that the hydrogen adjacent to the fluorine is highly labile.

Solid fluorourea was stable to prolonged storage at -20°, but aqueous solutions decomposed at ambient temperature, and an orange solid, identified as azodicarbondiamide began to deposit within 20 min. The same compound was formed from fluorourea in refluxing ethanol. However aqueous solutions of fluorourea with urea added gave no azodicarbondiamide, but, rather, a white solid which was shown to be biurea.



These reactions might take place by direct displacement of fluoride by the nucleophiles, fluorourea and urea, respectively, or through a cationic intermediate (or nitrene) resulting from initial loss of fluoride. The reaction of fluorourea with urea is in accord with the postulation of Glemser and Lüdemann.[2]

Fluorourea was also hydrolyzed with sulfuric acid, and the nature of the reaction varied greatly with the experimental conditions. A large excess of concentrated sulfuric acid at 40-50° gave fluor..mmonium ion, identified

by its NMR spectrum.[16] However, when a 2:1 mole ratio of concentrated sulfuric acid to fluorourea was used at 35°, hydrazine sulfate and ammonium sulfite were isolated. At 40°, an otherwise similar reaction resulted in a fume-off. The use of a large excess of 65% sulfuric acid at 60° also resulted in the isolation of ammonium sulfite. Fluorourea reacted with ketones and aldehydes in the presence of sulfuric acid to give amides and nitriles, respectively, the same products that were obtained from fluorammonium salts.[16]

The hydrolysis of fluorourea thus provides a reducing agent sufficiently powerful to reduce sulfuric acid. Possible structures for this reducing agent include fluoramine and its self-condensation product, diimide. It has been reported, however, that diimide does not reduce oxidized sulfur compounds.[17] Evidence has been presented that in the absence of an excess of strong acid, fluorammonium salts can dissociate to a small extent, to fluoramine in organic solvents.[16] Since difluoramine can function as a reducing agent,[18, 19] fluoramine would be expected to be a strong reducing agent, but other transient species could be involved. The reduction of sulfuric acid was also reported in the preparation of hydroxylamine from hydrazoic acid.[20]

The formation of the hydrazine salt is an example of the Raschig reaction which is unusual in that alkaline conditions are normally required. Hydrazine has been produced from chlorourea and base but the mechanism is not known.[21, 22]

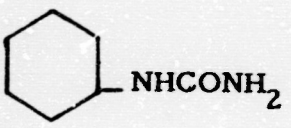
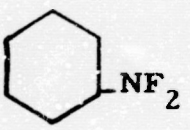
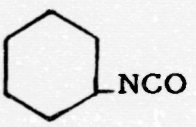
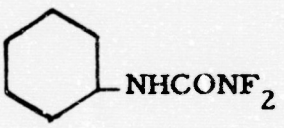
Only one report of the fluorination of substituted ureas has appeared. Banks, Haseldine and Lalu[14] reported that the aqueous fluorination of N, N'-dimethylurea gave difluoraminomethane and N-fluoro-N, N'-dimethylurea. N, N'-Diethylurea gave the analogous products but trimethylurea yielded only difluoraminomethane. Fluorinations of monosubstituted ureas have not been reported previously.

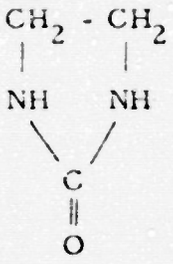
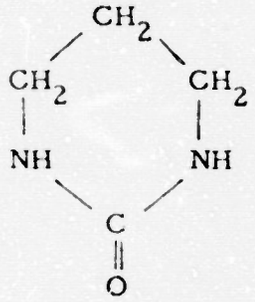
Results of the aqueous fluorination of monosubstituted ureas and cyclic disubstituted ureas in the present work are presented in Table I. The fluorination of simple alkylureas yielded difluoraminoalkanes and N-alkyl-N', N'-difluoroureas, and in the case of propylurea, the N-alkyl-N-fluorourea, a solid, was also isolated. The difluoraminoalkanes, difluoraminoethane,[23] 1-difluoraminopropane,[24] difluoraminocyclohexane[11] and 1, 3-bis(difluoramino)propane[7] were prepared previously by other methods. A mixture of ethyl difluoraminoacetate and its dehydrofluorination product, ethyl cyanoformate, was also isolated previously from the fluorination of ethyl N-carbomethoxyglycine.[7] The mixture could not be separated without further dehydrofluorination of ethyl difluoraminoacetate taking place.

The failure to isolate N, N'-difluoroureas is in accord with observations that in fluorinations of carbamates[6, 7] and amides,[8] monofluorinated products undergo further fluorination, with displacement of either hydrogens or acyl groups, more rapidly than the starting materials do. Thus the initial fluorination products of alkylureas are N-alkyl-N-fluoroureas and N-alkyl-N'-fluoroureas, which undergo further fluorination on

TABLE I

Fluorination of Substituted Ureas

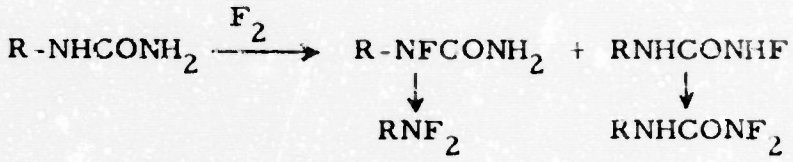
Starting Material	Products	bp(or mp), °C
$C_2H_5NHCONH_2$	$C_2H_5NF_2$	
	$C_2H_5NHCONF_2$	30-31(0.5 mm)
$CH_3CH_2CH_2NHCONH_2$	$CH_3CH_2CH_2NF_2$	45
	$CH_3CH_2CH_2NFCONH_2$	(78)
	$CH_3CH_2CH_2NHCONF_2$	40 (0.1 mm)
		35-42 (26 mm)[a]
		28-30 (0.1 mm)
		(59-60)
$C_2H_5OCCH_2NHCONH_2$ (O)	$C_2H_5OCCH_2NF_2$ (O)	32-42 (25 mm)
	C_2H_5OCCN (O)	
	$C_2H_5OCCH_2NHCONF_2$ (O)	66-67 (0.1 mm)

Starting Material	Products	bp (or mp), °C
	$NF_2CH_2CH_2NHCOF$	39-40 (0.05 mm)
	$NF_2CH_2CH_2CH_2NF_2$	38-50 (25 mm)[a]
	$NF_2CH_2CH_2C{\equiv}N$	58-60 (25 mm)[b]
	$NF_2CH_2CH_2CH_2NCO$	
	$NF_2CH_2CH_2CH_2NHCOF$	65-66 (0.1 mm)

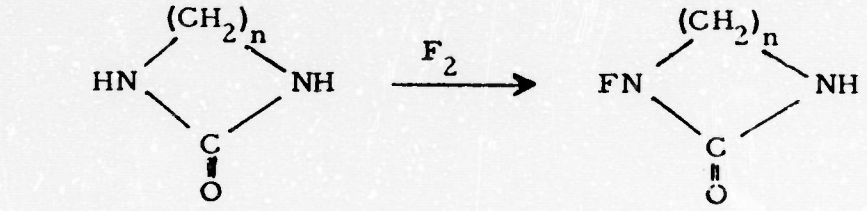
[a] Impure product identified by spectral comparison with an authentic sample.

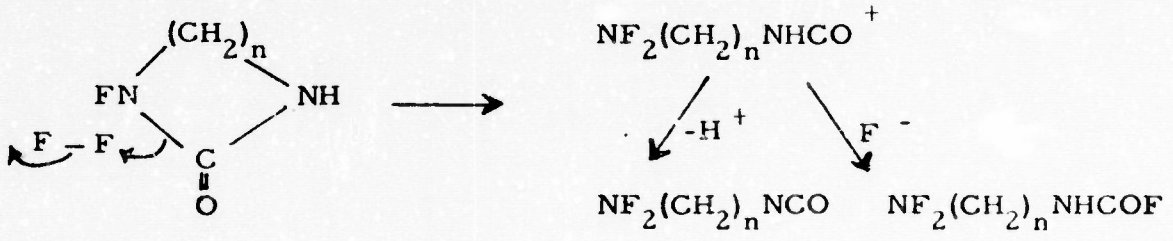
[b] Codistilled, separated by gas chromatography.

the same nitrogen to give alkyldifluoramines and N-alkyl-N', N'-difluoroureas, respectively. The second fluorination step takes place at the same nitrogen as the first, whether hydrogen or an acyl group is displaced.



The formation of carbamyl fluorides and isocyanate from the fluorinations of 2-imidazolidone and tetrahydropyrimidone are rationalized as electrophilic displacements of acylium ions from the monofluorinated intermediates. The resulting aminoacylium ions can react with fluoride to give the carbonyl fluorides or lose a proton to give isocyanate. This mechanism is similar to that postulated for the formation of ω-difluoramino-acid fluorides from the fluorination of lactams.[8]





n = 2 or 3

EXPERIMENTAL SECTION

General. - Fluorinations were conducted in a glass standard taper three-necked flask fitted with a mechanical stirrer, a glass tube extending below the liquid level used as a gas inlet, and a standard taper thermometer well with an opening for gas exit. The fluorine was diluted with 3 to 6 parts of nitrogen. Exit gases were vented through an aqueous potassium iodide trap. Safety shielding is required for the fluorinations and for handling compounds.

N, N-Difluorourea. - A solution of 60 g (1.0 mol) of urea in 800 ml of water was treated with 1 mol of diluted fluorine at 0-5° over an 8 hr period. The product was extracted with 4-200 ml portions of ether, dried over sodium sulfate, and a 5 % aliquot was stripped of solvent at 25 mm. The residue was dried for several minutes at 3 mm and was then sublimed at 0.1 mm onto a -78° condenser to give 3.55 g (74 % yield) of colorless platelets, mp 41-41.5°.[3]

Anal. Calcd for $CH_2N_2F_2O$: C, 12.50; H, 2.08; N, 29.17; F, 39.57. Found: C, 12.23; H, 2.35; N, 28.7; F, 38.8.

Fluorination of a suspension of 24 g (0.40 mol) of urea in 200 ml of acetonitrile (0.8 mol of fluorine, -15 to -20°, 2.5 hrs), removal of the bulk of solvent from a 25 % aliquot (25 mm), and recrystallization from methylene chloride and carbon tetrachloride gave 5.0 g (52 % yield) of white needles, mp 41-41.5°.

The two crystalline forms were interconvertible, and gave identical spectra in solution.[3, 14] The platelet form was quite hygroscopic, whereas the needle form was not.

Fluorourea. - A suspension of 60 g (1.0 mol) of urea in 300 ml of acetonitrile was fluorinated until a clear solution was formed (0.6 mol of fluorine, -5°). Addition of 500 ml of methylene chloride gave a heavy oil which was separated, washed with 50 ml of methylene chloride, and recrystallized from 2.5 liters of methylene chloride to give 25 g (53 % yield) of fluorourea, mp 56-57°.

Anal. Calcd for CH_3N_2OF: C, 15.39; H, 3.88; N, 35.89; F, 24.34. Found: C, 15.31; H, 4.20; N, 35.80; F, 23.7.

The proton NMR spectrum in tetrahydrofuran consisted of two broadened signals at ó 6.67 and 10.66 (area ratio 2:1), and the fluorine spectrum consisted of a singlet at +34.22 ppm from external trifluoroacetic acid.

The fluorination of aqueous urea (as in the N, N-difluorourea synthesis) with 1.0 mol of fluorine at 0-5° gave, after extraction with ether and recrystallization from methylene chloride, a 20 % yield of fluorourea.

Azodicarbondiamide. - A solution of 3.0 g (0.038 mol) of fluorourea in 20 ml of absolute ethanol was refluxed for 2.5 hrs and was then cooled to room temperature. The precipitate was filtered, washed with ethanol and ether to give 0.3 g of azodicarbondiamide, an orange solid, mp 260-265°(d).

From the filtrate 2.5 g of fluorourea was recovered on removal of the solvent.

A solution of 1.6 g (0.02 mol) of fluorourea in 25 ml of water was allowed to stand at ambient temperature. An orange precipitate began to form in 20 min. Azodicarbondiamide (0.1 g) was isolated after 5 days by filtration and washing with ethanol and ether.

Anal. Calcd for $C_2H_4N_4O_2$: C, 20.69; H, 3.45; N, 48.3. Found: C, 20.83; H, 3.34; N, 48.21.

Biurea. - An aqueous fluorourea solution as above containing 3.0 g (0.05 mol) of urea gave 0.4 g of biurea, a white solid, mp 265°(d).

Anal. Calcd for $C_2H_6N_4O_2$: C, 20.33; H, 5.08; N, 47.5. Found: C, 20.07; H, 5.02; N, 47.29.

Reaction of Fluorourea with Sulfuric Acid. - A solution of 0.3 g of fluorourea in 3.0 g of concentrated sulfuric acid was heated at 40 to 50° for 10 min. The fluorine nmr spectrum of the resulting solution was identical with that reported for fluorammonium bisulfate.[16]

A solution of 2.0 g (0.0026 mol) of fluorourea in 20 ml of 65 % sulfuric acid was heated at 60° until gas evolution ceased (1 hr). The solution was cooled to 25° and diluted with 50 ml of ethanol. A white solid separated, which was washed with ethanol and with ether and recrystallized from aqueous ethanol to give 1.5 g (30 % yield) of ammonium sulfite hydrate, mp 265-270°(d) (same mixed mp with an authentic sample), also identified by its ir spectrum.

A solution of 1.6 g (0.020 mol) of fluorourea in 4.0 g (0.04 mol) of concentrated sulfuric acid was heated at 35° with magnetic stirring. After 30 min foaming was observed and the mixture was cooled to 30° and 25 ml of ethanol was added. The precipitate was recrystallized from water to give 0.9 g of hydrazine sulfate, mp 254°. Dilution of the filtrate with 50 ml of ether and recrystallization of the resulting precipitate gave 0.85 g of ammonium sulfite hydrate. A similar reaction at 40° resulted in a fume-off.

Fluorination of Ethylurea. - Fluorination of 13.2 g (0.15 mol) of ethylurea in 350 ml of water (0-5°, 0.35 mol of fluorine) gave 6 g (49 % yield) of difluoraminoethane identified by its infrared spectrum.[23] The compound was isolated from the exit gas in a -78° trap and was purified by trap to trap distillation. Extraction of the aqueous solution with methylene chloride gave 3.0 g (16 % yield) of N, N-difluoro-N'-ethylurea, bp 30-31°(0.5 mm), n_D^{25} 1.3978.

Anal. Calcd for $C_3H_6N_2F_2O$: C, 29.04; H, 4.88; N, 22.58; F, 30.64. Found: C, 29.20; H, 5.15; N, 22.3; F, 29.5.

Fluorination of Propylurea. - Fluorination of 102 g (1.0 mol) of propylurea in 700 ml of water (1.5 mol fluorine, 6 hrs, 0-5°) gave 15 g (0.16 mol) of difluoraminopropane, bp 45°, which was condensed from the exit gas in a -78° trap.

Anal. Calcd for $C_3H_7NF_2$: C, 37.9; H, 7.4; N, 14.7; F, 39.95. Found: C, 37.8; H, 7.4; N, 14.7; F, 40.0.

The infrared spectrum showed bands in the NF region at (μ): 9.87 (m), 10.11 (m), 10.8 (sh), 11.0 (m), 11.34 (s) and 12.3 (vs).

The aqueous mixture was extracted with 5-50 ml portions of methylene chloride and 5-50 ml portions of ether. Distillation of the dried extracts gave 8.0 g (0.065 mol) of N, N-difluoro-N'-propylurea, bp 40° (0.1 mm), n_D^{25} 1.4045, and 4.0 g of N-fluoro-N-propylurea bp 40-50° (0.1 mm). Recrystallization of the latter from carbon tetrachloride gave 3.0 g (0.025 mol), mp 78°.

The proton nmr spectrum of N-fluoro-N-propylurea ($CDCl_3$ solution) consisted of a triplet at δ 0.99 for CH_3, a sextet at δ 1.74 for $CH_3\underline{CH_2}CH_2$-, a doublet of triplets (J_{HF} = 39.2 cps) at δ 3.66 for $CH_3\underline{CH_2}NF$ and a broad NH signal at δ 6.04. The fluorine spectrum consisted of a triplet (J = 39.7 cps) at ϕ^* + 66.7. The infrared spectrum showed carbonyl bands at 5.85 and 6.38 μ.

The proton nmr spectrum of N, N-difluoro-N'-propylurea (CCl_4 solution) consisted of a triplet at δ 0.99 for CH_3, a sextet at δ 1.65 for $CH_3\underline{CH_2}CH_2$, a slightly broadened quartet at δ 3.29 for $-CH_2\underline{CH_2}$-NH- and a broadened signal at δ 7.07 for NH. The fluorine spectrum consisted of a broadened singlet at ϕ^* -32.64 for NF_2.

Anal. Calcd for $C_4H_8NF_2O$: C, 34.78; H, 5.80; N, 20.3; F, 27.5. Found: C, 34.61; H, 5.90; N, 20.1; F, 27.8.

Fluorination of Cyclohexylurea. - Fluorination of a suspension of 27.6 g (0.20 mol) of cyclohexylurea in 600 ml of water (0.8 mol of fluorine, 0-5°), extraction with methylene chloride, and distillation gave 5.5 g of impure difluoraminocyclohexane,[11] by 35-42° (26 mm), 3.5 g of cyclohexyl isocyanate,[8] bp 28-30° (0.1 mm) and 9.0 g of crude N, N-difluorocyclohexylurea, bp 20-30° (0.1 mm). The latter crystallized in the receiver, and was recrystallized from heptane to give 8.3 g (25% yield) of white needles, mp 59-60°.

Anal. Calcd for $C_6H_{11}N_2F_2O$: C, 47.18; H, 6.79; N, 15.69; F, 21.33. Found: C, 46.83; H, 6.91; N, 15.4; F, 22.5.

The fluorine nmr spectrum (CCl_4 solution) consisted of a singlet at ϕ^* -32.8.

Fluorination of Ethyl Hydantoate. - Fluorination of a suspension of 73 g (0.50 mol) of ethyl hydantoate in 650 ml of water (1.0 mol fluorine, 2 hrs, 0-5°) and extraction with methylene chloride gave 17.0 g of a 45:55 mixture of ethyl cyanoformate and ethyl difluoraminoacetate,[7] bp 32-42° (25 mm) and 15 g (16.5% yield) of ethyl N, N-difluorohydantoate, bp 66-67° (0.1 mm).

Anal. Calcd for $C_5H_8N_2F_2O_3$: C, 32.97; H, 4.40; N, 15.4; F, 20.9. Found: C, 33.02; H, 4.50; N, 15.5; F, 20.7.

The proton nmr spectrum (CCl_4 solution) consisted of a triplet at δ 1.31 and a quartet at δ 4.20 for the ethyl, a doublet at δ 3.99 for -NH$\underline{CH_2}$CO-, and a broadened signal at δ 7.09 for NH. The fluorine spectrum consisted of a broadened singlet at ϕ^* -32.4.

Fluorination of 2-Imidazolidone. - A solution of 43 g (0.50 mol) of 2-imidazolidone in 650 ml of water was fluorinated (1.0 mol fluorine, 0-5°, 2 hrs), and extracted with 5-50 ml portions of methylene chloride. The product was treated with sodium sulfate and solid sodium bicarbonate and was distilled to give 18 g (25% yield) of 2-difluoraminoethylcarbamyl fluoride bp 39-40° (0.05 mm).

Anal. Calcd for $C_3H_5N_2F_3O$: C, 25.3; H, 3.55; N, 19.7; F, 40.1. Found: C, 25.4; H, 3.40; N, 19.5; F, 39.7.

The proton nmr spectrum ($CDCl_3$ solution) showed a broad NH signal at δ 5.93, and a triplet of triplets (J_{HF} = 29 cps) for $NF_2\underline{CH_2}CH_2$ at δ 3.71, the central member of which was overlapped by the other methylene signal. The fluorine spectrum showed a triplet (J = 27.5 cps) at ϕ^* -53.67 for NF_2 and a doublet (J = 7.4 cps) at ϕ^* + 14.73 for -NHCOF. The infrared spectrum showed NH (3.0 μ), C=) (5.6 μ) and bands in the NF region (μ) 10.3 (m), and 10.55 (m), 11.0 (w), 12.0 (s) and 12.5 (w).

Fluorination of Tetrahydro-2-pyrimidone. - A solution of 70 g (0.70 mol) of tetrahydro-2-pyrimidone in 650 ml of water was reacted with 3.0 mol of fluorine at 0 to 5°. The product was extracted with four 35 ml portions of methylene chloride and the resulting solution was dried over sodium sulfate, treated with solid sodium bicarbonate, filtered, and distilled through a 25 cm Holzmann column to give 8.0 g (6% yield) of 80% pure (gc analysis) 1,3-bis(difluoramino)propane,[7] bp 38-50° (25 mm), 9.5 g of a mixture containing 40% 3-difluoraminopropionitrile (5% yield) and

50% 3-difluoraminopropyl isocyanate (5% yield),[8] bp 58-60 (25 mm), and 25 g (21% yield) of 3-difluoraminopropylcarbamyl fluoride, bp 65-66° (0.1 mm). The nitrile and isocyanate were separated by gas chromatography (retention times, 35 min and 18 min, respectively, 8 ft x 0.25 in column of 10% diethyleneglycol adipate on Fluoropak 80, 100°, 50 cc He/min).

The proton nmr spectrum of 3-difluoraminopropionitrile (in 1:1 $CDCl_3$ CCl_4) consisted of a triplet (J = 8 cps) at δ 2.80 and a triplet of triplets (J_{HH} = 8 cps, J_{HF} = 26.9 cps) at δ 3.81. The fluorine spectrum showed a triplet at ϕ^* -51.66. The infrared spectrum showed C≡N at 4.45 μ (m) and bands in the NF region at (μ) 9.70 (m), 9.90 (m), 10.51 (s), 11.28 (m), 11.5 (w), 12.0 (s) and 12.7 (s).

Anal. Calcd for $C_3H_4N_2F_2$: C, 33.96; H, 3.80; N, 26.41; F, 35.84. Found: C, 33.70; H, 3.91; N, 26.3; F, 37.0.

The proton nmr spectrum of 3-difluoraminopropylcarbamyl fluoride ($CDCl_3$ solution) consisted of a quintet (J = 7 cps) at δ 1.98 for $CH_2\underline{CH_2}CH_2$, a broad signal at δ 5.68 for NH, a triplet of triplets (J_{HF} = 29.3 cps) at δ 3.58 for $NF_2\underline{CH_2}CH_2$ and a quartet at δ 3.34 for $CH_2\underline{CH_2}NH$. The fluorine spectrum showed a triplet (J = 28.5 cps) at ϕ^* -55.3 for NF_2 and a doublet (J = 7.3 cps) at ϕ^* + 14.59 (-NHCOF). The infrared spectrum showed NH at 3.0 μ and C=O at 5.60 μ.

Anal. Calcd for $C_4H_7N_2F_3O$: C, 30.77; H, 4.52; N, 17.95; F, 36.51. Found: C, 30.99; H, 4.60; N, 17.5; F, 36.0.

References

1. This work was supported by the Office of Naval Research and the Advanced Research Projects Agency.
2. O. Glemser and H. Lüdemann, Z. anorg. allgem. chem., 286, 168 (1956).
3. E. A. Lawton, E. F. C. Cain, D. F. Sheehan and M. Warner, J. Inorg. Nucl. Chem., 17, 188 (1961).
4. E. A. Lawton and J. Q. Weber, J. Am. Chem. Soc., 85, 3595 (1963).
5. Preliminary communication: V. Grakauskas, abstracts of the 140th meeting of the American Chemical Society, p. 23M (1961).
6. V. Grakauskas and K. Baum, J. Am. Chem. Soc., 91, 1679 (1969).
7. V. Grakauskas and K. Baum, "Direct Fluorination of Substituted Carbamates," J. Org. Chem., In press.
8. V. Grakauskas and K. Baum, "Direct Fluorination of Amides," J. Am. Chem. Soc., In press.
9. V. Grakauskas and K. Baum, J. Org. Chem., 33, 3080 (1968).
10. Tetrafluorourea has been prepared from difluorocarbamyl fluoride and alkali fluorides, G. W. Fraser and J. M. Shreeve, Inorg. Chem., 6, 1711 (1967).
11. K. Baum, J. Org. Chem., 32, 3648 (1967).
12. K. Baum, J. Am. Chem. Soc., 90, 7083 (1968).
13. T. E. Stevens and J. P. Freeman, J. Org. Chem., 29, 2279 (1964).
14. R. E Banks, R. N. Haszeldine, and J. P. Lalu, J. Chem. Soc. (C), 1966, 1514.
15. F. A. Johnson, Inorg. Chem., 5, 149 (1966).

16. V. Grakauskas, A. H. Remanick, and K. Baum, J. Am. Chem. Soc., 90, 3839 (1968).

17. For a review, see S. Hünig, H. R. Müller and W. Thier, Angew. Chem., Internat. Ed. 4, 271 (1965).

18. K. J. Martin, J. Am. Chem. Soc., 87, 394 (1965).

19. K. Baum, J. Org. Chem., 33, 4333 (1968).

20. K. F. Schmidt, Ber., 57, 704 (1924).

21. P. Shestakov, German Patent 164,755; P. Shestakov and V. Kind, Zh. Russ. Fiz. -Khim. Obshch, 40, 330 (1908).

22. P. A. S. Smith, "The Chemistry of Open-chain Organic Nitrogen Compounds," Vol. I, W. A. Benjamin, Inc., New York, 1965, p 274.

23. J. W. Frazer, J. Inorg. Nucl. Chem., 16, 63 (1960).

24. S. F. Reed, Jr. and R. C. Petry, Tetrahedron, 24, 5089 (1968).

APPENDIX B

Direct Fluorination of Amides[1]

Vytautas Grakauskas and Kurt Baum

Contribution of the Environmental Systems Division
Aerojet-General Corporation, Azusa, California

ABSTRACT

The fluorination of secondary amides was shown to be a general method for the synthesis of difluoramino compounds and N-alkyl-N-fluoroamides. Formation of difluoramino compounds by the displacement of acylium ions was evidenced by the isolation difluoraminoacids from lactams and 2-difluoraminoethanol esters from N-acylethanolamines. Some chemical properties of difluoraminoacids are described. Alkylfluorammonium salts were prepared by the reaction of N-alkyl-N-fluoroamides with sulfuric acid. The fluorination of cyclohexanecarboxamide gave cyclohexyl isocyanate and cyclohexyl carboxylic acid, apparently by hydrolysis of the difluoroamide. Oxidation of the fluorination product of acetamide gave tetrafluorohydrazine.

The direct fluorination of alkyl carbamates results in replacement of one or both hydrogens on nitrogen by fluorine,[2] whereas the fluorination of alkyl N-alkylcarbamates results in replacement of NH and subsequently acyl groups.[3] Fluorination studies of amides[4] have been limited to acetamide and N-methylacetamide. Aqueous fluorination of acetamide was reported to give only acetic acid, carbon dioxide, nitrous oxide and a trace of tetrafluor hydrazine, and that of N-methylacetamide was reported to give acetic acid, carbon dioxide and a 7% yield of difluoraminomethane. The present paper describes the fluorination of a variety of amides to give N-fluoroamides and difluoraminoalkanes, as well as rearrangement products.

Products of the fluorination of secondary amides are shown in Table I. The fluorinations were generally conducted using solutions or suspensions of the substrates in water or acetonitrile, although in several cases no solvent was used. The reactions are similar to those of carbamates in that successive fluorination of NH and fluorinolysis of acyl groups takes place. The rates of the two reactions are of the same order of magnitude, and considerable amounts of difluoraminoalkanes are formed, even at low fluorine to substrate ratios. The reactions, however, are characterized by high selectivity toward nitrogen and only two CH fluorination products, 1,3-bis(difluoramino)-1-fluoropropane and 2-difluoraminoethyl fluoroacetate, were isolated in this work. As a practical synthesis method for difluoramino-alkanes, the fluorination of secondary amides is comparable to that of carbamates, and therefore provides a more convenient choice of starting materials. The intermediates, N-fluoroamides are isolated readily by

TABLE I

Fluorination of Secondary Amides

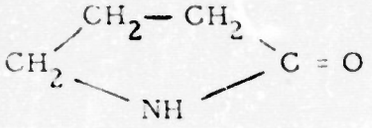
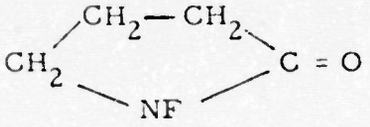
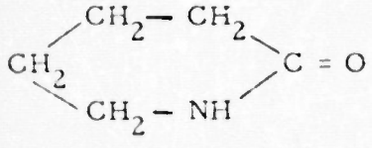
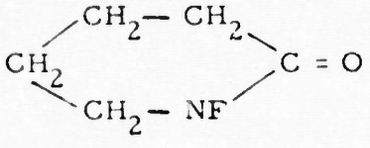
Starting Material	Products	bp, °C
CH_3NHCHO	CH_3NFCHO	76-77[a]
	CH_3NF_2	b
C_2H_5NHCHO	C_2H_5NFCHO	21-22 (25 mm)
	$C_2H_5NF_2$	b
$CH_3(CH_2)_3NHCOCH_3$	$CH_3(CH_2)_3NFCOCH_3$	45-46[a]
$CH_3CONHCH_2CH_2CO_2H$	$NF_2CH_2CH_2CO_2H$	60 (1 mm)
		37-38 (0.15 mm)
	$NF_2(CH_2)_3COOH$	52-54 (0.15 mm)
	$NF_2(CH_2)_3COF$[c]	<20 (0.2 mm)[a]
		60-62 (0.2-0.3)
	$NF_2(CH_2)_4COOH$	d

TABLE I (Cont'd)

Starting Material	Products	bp, °C
$HCONH(CH_2)_3NHCHO$	$NF_2(CH_2)_3NF_2$	26-30 (25 mm)[a]
	$NF_2CHF(CH_2)_2NF_2$	
	$NF_2(CH_2)_3NFCHO$	31-32 (0.2-0.3 mm)[a]
$HCONHCH_2CH_2OH$	$NF_2CH_2CH_2OCHO$	38-45 (25 mm)
	$NF_2CH_2CH_2OH$	
$CH_3CONHCH_2CH_2OH$	$NF_2CH_2CH_2OCOCH_3$	40-50 (25 mm)[a]
	$NF_2CH_2CH_2OH$	
	$NF_2CH_2CH_2OCOCH_2F$	29-30 (0.1 mm)[a]

[a] Impure distillate; analytical sample was isolated by gas chromatography.

[b] Spectroscopic identification.

[c] Nonhydrolytic fluorination conditions.

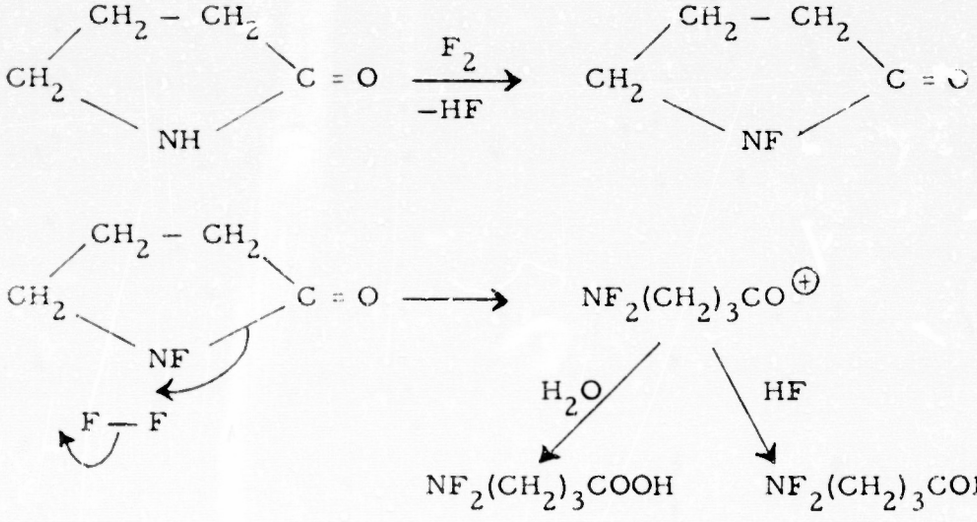
[d] Purified through salt formation.

conventional methods.

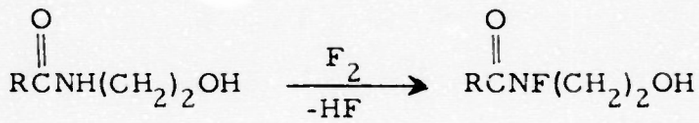
$$RNHCR' \xrightarrow{F_2} RNFCR' \xrightarrow{F_2} RNF_2$$

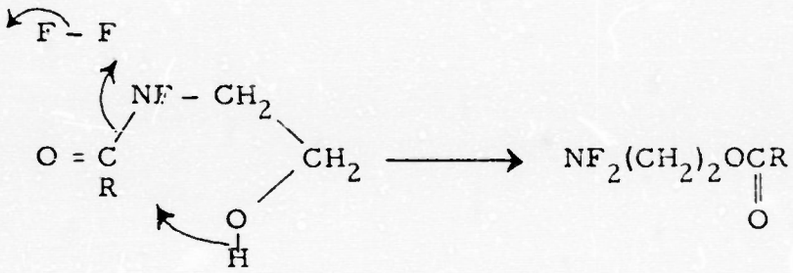
The products were characterized by elemental analysis and spectral data, or by comparison with authentic samples. Methyldifluoramine and ethyldifluoramine were prepared previously by reactions of N_2F_4 with alkyl iodides.[5] β-Difluoraminopropionic was prepared previously by the addition of difluoramine to acrylic acid,[6] and 1, 3-bis(difluoramino)propane, and 2-difluoraminoethanol, by the fluorination of the corresponding carbamates.[3]

The fluorinolysis of acyl groups can be rationalized as an electrophilic displacement of acylium ions by fluorine. In the case of lactams, the acyl fragment is retained in the product molecule. For example, 2-pyrrolidinone gave 3-difluoraminobutyric acid in aqueous solution, and 3-difluoramino-butyryl fluoride when no solvent was used in the fluorination.



Further evidence for electrophilic acylium ion displacement is found in the fluorinations of N-acylethanolamines. The fluorinations of both the formyl and acetyl derivatives in aqueous solution gave 2-difluoramino-ethanol and its corresponding esters. In the case of the acetyl compound, the fluoroacetate was also isolated. The alcohol function thus competes with the solvent to trap acylium ions.





R = H, CH_3

Simple N-fluoro-N-alkylamides were found to be hydrolytically stable in the presence of dilute aqueous acid. They underwent hydrolysis in concentrated sulfuric acid under the same conditions as the corresponding carbamates.[7] Thus methyl-N-fluoroformamide gave the previously identified[7] methylfluorammonium ion. Ethyl-N-fluoroformamide gave ethylfluorammonium ion. The fluorine nmr spectrum of the sulfuric acid solution, a triplet of triplets at -15.51 ppm from external trifluoroacetic acid (J_{NH_2-F} = 42.5 cps, J_{CH_2-F} = 28.7 cps) was consistent with previously reported fluorammonium

ion spectra.[7]

$$RNFCHO \xrightarrow[\Delta]{H_2SO_4} RNH_2F^{\oplus}\ HSO_4^{\ominus}$$

Although primary difluoramino compounds have been reported to undergo facile dehydrofluorination in the presence of bases,[8] it was found that analytically pure 6-difluoraminohexanoic acid could be isolated in 46% overall yield by extraction of the ϵ-caprolactam fluorination mixture with cold bicarbonate solution. On the other hand aqueous sodium hydroxide at 0 to 3° reacted with the acid to give a 59% yield of 5-cyanovaleric acid in 15 min. Reactions of 6-difluoraminohexanoic acid and 4-difluoraminobutyric acid with alcohols in the presence of a trace of acid gave high yields of the corresponding esters.

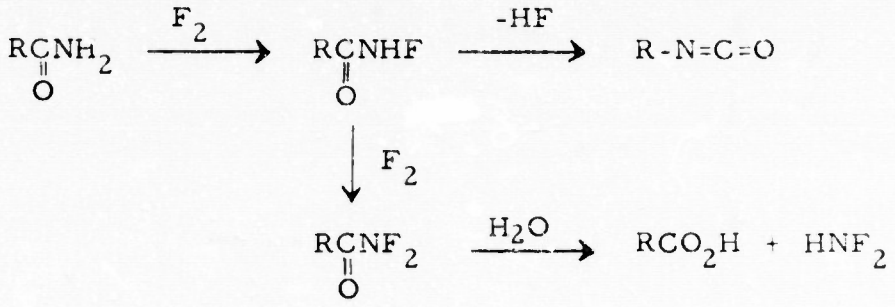
3-Difluoraminobutyric acid reacted with thionyl chloride to give the acid chloride or the anhyride depending on the reactant ratio. The acid chloride reacted with sodium azide in benzene to give an 85% yield of the isocyanate. The isocyanate reacted with ethanol to give ethyl N-(3-difluoraminopropyl)carbamate, a compound previously obtained in impure form from the fluorination of ethyl trimethylenedicarbamate.[3]

$$NF_2(CH_2)_3COOH \xrightarrow{SOCl_2} NF_2(CH_2)_3COCl$$

$$\xrightarrow[\Delta]{NaN_3,\ C_6H_6} NF_2(CH_2)_3NCO \xrightarrow{EtOH} NF_2(CH_2)_3NHCO_2Et$$

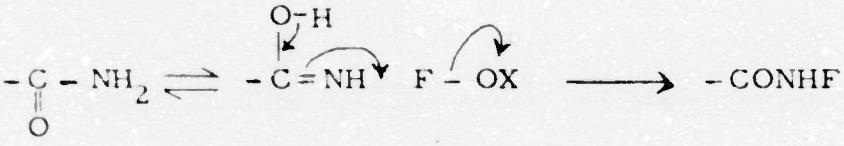
A more limited study was made of fluorinations of primary amides. The expected initial products, N-fluoroamides, could be expected to undergo further fluorination to give N, N-difluoroamides. Another possible reaction path of N-fluoroamides leads to isocyanates by the Hofmann rearrangement. Isocyanates have been isolated from reactions of primary amides with iodine pentafluoride,[9] and similar nucleophilic rearrangements were observed in reactions of fluorammonium salts with carbonyl compounds. N, N-Difluoroamides were prepared previously from tetrafluorohydrazine and acyl radical sources,[10] and were reported to react readily with hydroxylic compounds; reactions with HF, the fluorination byproduct, would therefore be expected.

Fluorination of cyclohexanecarboxamide in acetonitrile with two moles of fluorine gave an 18% yield of cyclohexyl isocyanate and a 48% yield of cyclohexanecarboxylic acid (after aqueous bicarbonate extraction). The starting material was not hydrolyzed by HF under the fluorination conditions in a control experiment, indicating that the difluoroamide is a precursor to the acid. Additional evidence for a difluoroamide intermediate was obtained by fluorinating acetamide in acetonitrile and oxidizing the solution with chromic acid; a 50% yield of tetrafluorohydrazine was isolated. Tetrafluorohydrazine has been prepared from difluorocarbamates by this method.[11]



Banks, Haszeldine and Laln[4] have proposed a mechanism for the formation of alkyldifluoramines from carbamates and amides in which fluorine adds to the carbonyl group of the N-fluoro intermediate followed by intramolecular fluorination by the OF, e.g.,

For the first step of the fluorinations in aqueous solutions, they proposed the reaction of oxygen difluoride or hypofluorous acid with the enolic forms of the substrates, e.g.,



There now appears to be no reason to invoke oxygen difluoride or hypofluorous acid as intermediates, since similar results (aside from product hydrolysis) are obtained with water or acetonitrile as fluorination solvents. Enolization of the substrates is unnecessary since simple amines can be fluorinated in buffered aqueous solutions,[12] and weakly basic amines, in liquid HF.[13] There is no evidence of fluorine addition to carbonyl groups in the uncatalyzed fluorination of simple esters.[14] The displacement of acylium ions is well known with other electrophilic reagents. The simplest mechanism consistent with the available experimental data is the electrophilic displacement of hydrogen and acylium ions by molecular fluorine.

EXPERIMENTAL SECTION

General. - Fluorinations were conducted in a glass standard taper three-necked flask fitted with a mechanical stirrer, a glass tube extending below the liquid level used as a gas inlet, and a standard taper thermometer well with an opening for gas exit. Standard fluorine-handling hardware[15] was used, and the fluorine was diluted with nitrogen. Exit gases were vented through an aqueous potassium iodide trap. Safety shielding is required for the fluorinations and for handling NF compounds.

Methyl-N-fluoroformamide. - Methylformamide (100 g, 1.7 mol) was fluorinated without a solvent with 0.67 mol of fluorine at -30 to -40° over a 2.5 hr period. A mixture of methyldifluoramine[5] and hydrogen fluoride (12 g, ir identification) was removed at 10-15° (25 mm), and the remaining product was vacuum transferred at 25° (0.2 mm) into a -80° receiver. Distillation of the condensate gave 18.0 g (31 % yield) of 93 % pure (gc analysis) methyl-N-fluoroformamide, bp 76-77°. An analytical sample was isolated by gas chromatography (10 ft x 0.25 in column of 25% butyl phthalate on Chromosorb P, 75°, 50 cc/min He), which showed four more volatile compounds.

Anal. Calcd for C_2H_4NFO: C, 31.17; H, 5.23; N, 18.18; F, 24.66. Found: C, 31.31; H, 5.39; N, 18.0; F, 24.1.

The proton nmr spectrum ($CDCl_3$ solution) showed a doublet (J = 26.2 cps) at δ 3.45 for the methyl and a doublet (J = 13 cps) at δ 8.58 for -CHO. The fluorine spectrum showed a broad signal at ϕ^* + 67.1. The infrared spectrum showed the following peaks (μ): 3.45 (ω), 5.86 (s), 6.74 (ω), 7.0 (ω), 7.60 (m),

8.70 (m), 9.0 (m), 9.69 (m), 9.9 (sh) and 12.2 (s).

When the fluorination was conducted in aqueous solution only methyldifluoramine was obtained.

Ethyl-N-fluoroformamide. - A solution of 73 g (1.0 mol) of ethylformamide in 350 ml of water was treated with 1 mol of fluorine at 0 to 5°. Ethyldifluoramine (4.5 ml) identified by its infrared spectrum,[5] was collected in a -80° trap in series with the fluorination flask. The aqueous layer was extracted with three 100 ml portions of ether, dried, and distilled to give 5.0 g (5.5 % yield) of ethyl-N-fluoroformamide, bp 20-21° (25 mm), n_D^{25} 1.3930.

Anal. Calcd for C_3H_6NFO: C, 39.55; H, 6.64; N, 15.38; F, 20.86. Found: C, 39.60; H, 6.81; N, 15.4; F, 21.1.

The proton nmr spectrum ($CDCl_3$ solution) consisted of a triplet (J = 7.5 cps) at δ 1.31 for the methyl, a doublet (J_{HF} = 31.2 cps) of quartets (J_{HH} = 7.5 cps) at δ 3.84 for the methylene and a doublet (J_{HF} = 13.3 cps) at δ 8.53 for -CHO. The fluorine spectrum showed a broad unresolved signal at ϕ^* + 81.7. The infrared spectrum showed a carbonyl band at 5.8 μ and an NF band at 10.5 μ.

The fluorination of 100 g (1.37 mol) of ethylformamide (no solvent) with 0.32 mol of diluted fluorine at -40 to -45° over a 2.5 hr period gave 4 ml of ethyldifluoramine and 12.0 g (41% yield based on fluorine) of ethyl-N-fluoroformamide.

Butyl-N-fluoroacetamide. - A solution of 86.5 g (0.75 mol) of butylacetamide in 450 ml of water was fluorinated with 0.75 mol of fluorine at 0 to 5°. The product was extracted with three 50 ml portions of methylene chloride, dried over sodium sulfate, and distilled to give 2.0 g (1.5 % yield) of 75 % pure butyl-N-fluoroacetamide, bp 45-46° (25 mm). An analytical sample was prepared by gas chromatography (6 ft x 0.25 in. column of 10 % UCON 50 HB100 on Fluoropak 80, 115°, 75 cc/min He, retention time 28 min).

Anal. Calcd for $C_6H_{12}NFO$: C, 54.12; H, 9.08; N, 10.52; F, 14.27. Found: C, 54.00; H, 9.11; N, 10.8; F, 14.6.

The proton nmr spectrum (CCl_4 solution) showed an irregular triplet at δ 0.95 for $-CH_2\underline{CH_3}$, a doublet of triplets at δ 3.73 (J_{HF} = 33.8 cps) for $-NF-\underline{CH_2}CH_2-$, a multiplet at δ 1.5 for the other methylenes, and a doublet (J_{HF} = 7.6 cps) at δ 2.12 for $\underline{CH_3}CONF-$. The fluorine spectrum consisted of a triplet (J = 33.8 cps) of quartets (J = 7.3 cps) at ϕ^* + 66.37. The infrared spectrum showed a carbonyl at 5.90 μ and relatively weak bands in the NF region at 10.01, 10.5, 11.0 and 11.4 μ.

β-Difluoraminopropionic Acid. - Fluorination of 26.2 g (0.20 mol) of water (0.4 mol of fluorine, 5 hr), extraction with ether, drying over Drierite, and distillation gave 9.0 g (36 % yield) of β-difluoraminopropionic acid, identical with that prepared previously.[6]

Fluorination of 2-Pyrrolidinone. - A solution of 85 g (1.0 mol) of 2-pyrrolidinone in 1 liter of water was treated with 1.0 mol of fluorine.

(0 to 5°, 1.5 hr). The product was extracted with five 75 ml portions of methylene chloride, dried and distilled to give 17 g (16.5 % yield) of N-fluoro-2-pyrrolidinone, bp 37-38° (0.15 mm), n_D^{25} 1.4390 and 15 g (11 % yield) of 4-difluoraminobutyric acid, bp 52-54° (0.15 mm), n_D^{25} 1.4150, with spectra identical with those reported previously.[3]

The infrared spectrum of N-fluoro-2-pyrrolidinone showed a carbonyl band at 5.73 μ and bands in the NF region at 10.0 μ (s), 10.35 μ (ω) and 11.18 μ (ω). The proton nmr spectrum (CCl_4 solution) consisted of a doublet (J_{HF} = 9.6 cps) of irregular triplets at δ 3.67 for $-CH_2-NF-$ and a multiplet at δ 2.25 for the other methylenes. The fluorine spectrum consisted of a broad signal at ϕ^* + 71.2.

Anal. Calcd for C_4H_6NFO: C, 46.60; H, 5.87; N, 13.57; F, 18.43. Found: C, 46.22; H, 5.70; N, 13.4; F, 18.9.

In another experiment, 140 g (1.65 mol) of 2-pyrrolidinone was fluorinated with no solvent (0.5 mol of fluorine, 2.5 hr, 0 to 5°). Some localized ignition at the inlet and charring took place. Volatile products were vacuum transferred at ambient temperature into a -80° receiver. Distillation of the condensate gave 12.5 g (24% yield) of N-fluoro-2-pyrrolidinone, bp 38-39° (0.2 mm). The forecut of this distillation, bp<20° (0.2 mm), 1.5 g, was found by gas chromatography (14 ft x 0.25 in. column of 10 % diethyleneglycol adipate on Fluoropak 80, 80°, 50 cc He/min) to consist of 95 % 3-difluoramino-butyryl fluoride. An analytical sample was isolated by gas chromatography.

Anal. Calcd for $C_4H_6NF_3O$: C, 34.05; H, 4.29; N, 9.93; F, 40.39. Found: C, 34.20; H, 4.23; N, 10.05; F, 39.2.

The proton nmr spectrum (CCl_4 solution) consisted of a triplet of triplets at δ 3.58 (J_{HF} = 28.9 cps) for $NF_2\underline{CH_2}$-, a quintet at δ 2.08 for $CH_2\underline{CH_2}CH_2$ and a triplet at 2.68 for $-\underline{CH_2}\overset{O}{\overset{\|}{C}}-$. The fluorine spectrum consisted of a triplet at ϕ^* -54.16 for NF_2 and a signlet at ϕ^* -43.87 for $-\overset{O}{\overset{\|}{C}}F$. The infrared spectrum showed a carbonyl band at 5.48 μ and bands in the NF region at 9.85 (m), 10.3 (m), 11.0 (m), 11.37 (m), 11.6 (m) and 12.3 μ (s).

N-Fluoro-ϵ-caprolactam. – A solution of 113 g (1.0 mol) of ϵ-caprolactam in 1 liter of water was treated with 1.0 mol of fluorine (0 to 5°, 3 hrs). The product was extracted with four 75 ml portions of methylene chloride, and the methylene chloride solution was extracted with cold aqueous sodium bicarbonate solution. The methylene chloride solution was dried and distilled to give 26 g (20 % yield) of N-fluoro-ϵ-caprolactam, bp 60-62° (0.2 to 0.3 mm), n_D^{25} 1.4640.

Anal. Calcd for $C_6H_{10}NFO$: C, 54.94; H, 7.69; N, 10.68; F, 14.49. Found: C, 54.61; H, 7.52; N, 10.2; F, 15.0.

The proton nmr spectrum (CCl_4 solution) consisted of a doublet of triplets (J_{HF} = 28.5 cps) at δ 3.89 for $\underline{CH_2}NFCO$-, a multiplet at δ 2.4 for $-CH_2-CO-$ and a multiplet at 1.77 for the other methylenes. The fluorine spectrum consisted of a triplet (J = 29.6 cps) at ϕ^* + 44.0. The infrared spectrum showed a carbonyl band at 5.88 μ and bands in the NF region at

9.8 (ω), 10.18 (s), 10.42 (m), 10.70 (s), 11.82 (s), 12.4 (m) and 12.6 μ (s).

The distillation residue contained ϵ-caprolactam, and acidification of the bicarbonate solution gave 6-difluoraminohexanoic acid.

6-Difluoraminohexanoic Acid. - A solution of 56.5 g (0.50 mol) of ϵ-caprolactam in 650 ml of water was treated with 1.0 mol of fluorine at 0 to 5°. The product was extracted with ether and the ether solution was extracted with sodium bicarbonate solution at 0 to 5°. The sodium bicarbonate solution was acidified with sulfuric acid, and the product was extracted with methylene chloride, dried, and stripped of solvent to give 40 g (46 % yield) of 6-difluoraminohexanoic acid. Unreacted ϵ-caprolactam was recovered from the ether layer.

Anal. Calcd for $C_6H_{11}NF_2O_2$: C, 43.12; H, 6.63; N, 8.4; F, 22.7. Found: C, 43.47; H, 6.24; N, 8.3; F, 21.9.

The proton nmr spectrum (CCl_4 solution) consisted of a triplet of triplets (J_{HF} = 30 cps, J_{HH} = 8 cps) at δ 3.52 for NF_2-$\underline{CH_2}$-, multiplets at δ 1.75 and δ 2.4 for the other methylenes, and a singlet at δ 12.20 for -COOH. The fluorine spectrum consisted of a triplet (J = 30 cps) of doublets (J = 7 cps) at ϕ^* -55.7. The infrared spectrum showed broad OH-CH absorption at 3 to 4 μ, carbonyl at 5.88 μ and bands in the NF region at 9.8, 10.75, 11.0 and 11.7 μ.

Fluorination of N, N'-Diformyl-1, 3-diaminopropane. - Fluorination of 26 g (0.20 mol) of N, N'-diformyl-1, 3-diaminopropane in 350 ml of water (0.8 mol of fluorine, 0 to 5°), extraction with methylene chloride, and

distillation gave 2.5 g of colorless liquid, b.p. 26-30° (25 mm). Gas chromatography (6 ft x 0.25 in column of 10 % dioctyl phthalate on Fluoropak 80, 70°) showed that the sample contained, in the order of elution, 33 % (2.5 % yield) 1,3-bis(difluoramino)-1-fluoropropane and 55 % (5.6 % yield) 1,3-bis(difluoramino)propane. The latter was identified by its spectra.[3]

The proton nmr spectrum of 1,3-bis(difluoramino)-1-fluoropropane (CCl_4 solution) consisted of a triplet of triplets (J_{HF} = 27.6 cps) at δ 3.73 for $NF_2\underline{CH_2}CH_2$-, a broad multiplet at δ 5.45 for the methine, and a multiplet at δ 2.27 for the other methylene. The fluorine spectrum consisted of a poorly resolved triplet (J ~ 25 cps) at ϕ^* -53.37 for NF_2-CH_2-, a broadened AB quartet (ϕ^*_A = -29.2, ϕ^*_B = -19.3, J_{AB} = 610 cps) for $CHF\underline{NF_2}$, and a doublet (51 cps) of triplets (19 cps) at ϕ^* + 173.41 for -$CH_2\underline{CHF}$-. Lack of observable coupling between adjacent CF and NF_2 groups has been observed previously.[3]

Anal. Calcd for $C_3H_5N_2F_5$: C, 21.95; H, 3.05; N, 17.05; F, 57.9. Found: C, 21.67; H, 3.31; N, 16.2; F, 56.2.

In another experiment, the fluorination of 130 g (1.0 mol) of N,N'-diformyl-1,3-diaminopropane (no solvent, 1.5 mol of fluorine) was carried out at 10 to 20° over a 6.5 hrs period. The mixture was washed with water, dried and distilled to give 8 g of impure, 1,3-bis(difluoramino)propane and 4.0 g of N,N,N'-trifluoro-N'-formyl-1,3-diaminopropane, bp 31-32° (0.2-0.3 mm), of approximately 95 % purity. An analytical sample was obtained

by gas chromatography.

Anal. Calcd for $C_4H_7N_2F_3O$: C, 30.77; H, 4.52; N, 17.94; F, 36.51. Found: C, 30.41; H, 4.60; N, 18.0; F, 36.6.

The proton nmr spectrum (CCl_4 solution) showed a quintet (J = 8 cps) at δ 2.14 for $CH_2\underline{CH_2}CH_2$, a triplet of triplets (J_{HF} = 28.7 cps, J_{HH} = 8 cps) at δ 3.61 for $NF_2\underline{CH_2}CH_2$, a doublet (J_{HF} = 32.6 cps) of triplets at δ 3.92 for $CH_2\underline{CH_2}NF$-, and a doublet (J = 11.3 cps) at δ 8.59 for CHO. The fluorine spectrum consisted of a triplet (J = 32 cps) of doublets (J = 11 cps) at ϕ^* + 79.1 for $CH_2\underline{NF}CHO$ and a triplet (J = 28 cps) at ϕ^* -54.6 for NF_2.

Fluorination of N-Formylethanolamine. - The product of fluorination of 44.5 g (0.5 mol) of N-formylethanolamine (350 ml of water, 1 mol of fluorine, 0 to 5°, 2 hrs) was extracted with five 25 ml portions of methylene chloride, dried over sodium sulfate, treated with solid sodium bicarbonate, and distilled to give 17.5 g of liquid, bp 38-45° (25 mm). Gas chromatography indicated a mixture consisting of 11 % 2-difluoraminoethanol and 89 % 2-difluoraminoethyl formate

The infrared spectrum of the latter showed carbonyl at 5.85 μ and bands in the NF region at 9.77 (m), 10.34 (s), 11.22 (ω), 11.9 (s) and 12.5 μ (s).

Anal. Calcd for $C_3H_5NF_2O_2$: C, 28.8; H, 4.03; N, 11.2; F, 30.4. Found: C, 28.7; H, 4.15; N, 11.2; F, 30.4.

A solution of 10.0 g of the above mixture in 15 ml of methanol con-

taining a drop of sulfuric acid was heated at 55-60° for 2 hrs and then distilled to give 6.1 g of 90 % 2-difluoraminoethanol.

Fluorination of N-Acetylethanolamine. - The product of fluorination of 103 g (1.0 mol) of N-acetylethanolamine (650 ml of water, 2 mol of fluorine, 0 to 5°) was extracted with five 40 ml portions of methylene chloride, dried over sodium sulfate, treated with solid sodium bicarbonate and distilled to give 23 g of colorless liquid, bp 40-50° (25 mm) and 5.0 g, bp 29-30° (0.1 mm). Gas chromatography showed that the 23 g fraction contained 15 % 2-difluoraminoethanol (3.6 % yield) and 80 % 2-difluoraminoethyl acetate (13 % yield), and that the 5 g portion contained 69 % of an unidentified non-fluorinated compound and 26 % 2-difluoraminoethyl fluoroacetate (0.8 % yield). Analytical samples were prepared by gas chromatography.

The proton nmr spectrum of 2-difluoraminoethanol ($CDCl_3$ solution) consisted of a singlet at δ 2.25 for the hydroxyl and multiplets for the methylenes. The fluorine spectrum consisted of a triplet ($J = 26$ cps) at ϕ^* -54.88. The infrared spectrum showed prominent bands at 3.0, 9.28, 9.56, 10.43, 11.1, 11.9, and 12.61 μ.

Anal. Calcd for $C_2H_5NF_2O$: C, 24.75; H, 5.16; N, 14.44; F, 39.15. Found: C, 24.59; H, 5.30; N, 14.3; F, 38.5.

The proton nmr spectrum (CCl_4 solution) of 2-difluoraminoethyl acetate consisted of a singlet at δ 2.04 for $-\overset{\overset{O}{\|}}{C}CH_3$, a triplet of triplets ($J_{HF} = 28$ cps, $J_{HH} = 7$ cps) at δ 3.70 for $NF_2\underline{CH_2}CH_2$ and a multiplet at δ 4.2

for the other methylene. The fluorine spectrum showed a triplet (J = 25 cps) at ϕ^* -54.57. The infrared spectrum showed carbonyl at 5.78 μ.

Anal. Calcd for $C_4H_7NF_2O_2$: C, 34.54; H, 5.07; N, 10.07; F, 27.3. Found: C, 34.40; H, 5.16; N, 9.87; F, 27.8.

The proton nmr spectrum of 2-difluoraminoethyl fluoroacetate (CCl_4 solution) consisted of a triplet of triplets (J_{HF} = 25 cps, J_{HH} = 6 cps) at δ 3.78 for $NF_2\underline{CH_2}CH_2$, a triplet (J = 7 cps) at δ 4.58 for $-\underset{O}{\overset{\|}{C}}\underline{CH_2}-$, and a doublet (J = 46.4 cps) at δ 4.83 for CH_2F-. The fluorine spectrum showed a triplet (J = 27 cps) at ϕ^* -54.2 for NF_2 and a triplet (J = 46.7 cps) at ϕ^* + 231.7 for CF.

Anal. Calcd for $C_4H_6NF_3O_2$: C, 30.57; H, 3.85; N, 8.92; F, 36.3. Found: C, 30.96; H, 3.65; N, 9.07; F, 35.5.

Ethylfluorammonium Bisulfate. - A solution of 0.4 g of ethyl-N-fluoroformamide in 2 g of concentrated sulfuric acid was heated at 65 to 70° for 45 min; gas evolution began at 45°. The fluorine nmr spectrum, which consisted of a triplet (J_{NH-F} = 42.5 cps) of triplets (J_{CH-F} = 28.7 cps) at -15.51 ppm from external trifluoroacetic acid, was consistent with those of previously reported fluorammonium salts.[7]

Methylfluorammonium Bisulfate. - The above procedure using methyl-N-fluoroformamide gave a methylfluorammonium bisulfate solution in sulfuric acid identified by nmr spectra.[7]

5-Cyanovaleric Acid. - A solution of 5 g of sodium hydroxide in 20 ml

of water was added dropwise over a 15 min period to a solution of 5.0 g (0.030 mol) of 6-difluoraminohexanoic acid in 25 ml of water at 0 to 3°. The solution was then allowed to stand at ambient temperature for 15 min and was acidified with sulfuric acid. The product was extracted with three 20 ml portions of methylene chloride, dried and distilled to give 2.0 g (59 % yield) of 5-cyanovaleric acid with the reported physical properties.[16]

Ethyl 6-Difluoraminohexanoate. - A solution of 3.8 g (0.023 mol) of 6-difluoraminohexanoic acid in ethanol containing 0.1 ml of sulfuric acid was refluxed for 8 hrs. Ice (100 g) was added and the product was extracted with methylene chloride and distilled to give 3.5 g (78 % yield) of ethyl 6-difluoraminchexanoate, bp 49-50° (0.2 mm), n_D^{25} 1.4060.

Anal. Calcd for $C_8H_{15}NF_2O_2$: C, 49.2; H, 7.74; N, 7.17; F, 19.5. Found: C, 48.9; H, 7.2; N, 7.10; F, 19.8.

The proton nmr spectrum (CCl_4 solution) consisted of a triplet at δ 1.23 and a quartet at δ 4.05 for CH_3CH_2-O- , a triplet of triplets (J_{HF} = 29 cps), J_{HH} = 7 cps) at 3.43 for $NF_2\underline{CH_2}$-, and multiplets at δ 1.57 and δ 2.25 for the other methylenes. The fluorine spectrum consisted of a triplet (J = 30 cps) at ϕ^* -55.8. The infrared spectrum showed carbonyl at 5.8 u and weak bands in the NF region at 10.3, 10.8, 11.1 and 11.65 μ.

Similarly, methyl 6-difluoraminohexanoate and ethyl γ-difluoraminobutyrate was prepared, bp 45-46° (0.2 mm), n_D^{25} 1.4050, and bp 26-27° (0.2 mm), n_D^{25} 1.3932, respectively.

Anal. Calcd for $C_7H_{13}NF_2O_2$: C, 46.41; H, 7.20; N, 7.7; F, 21.0. Found: C, 46.12; H, 7.10; N, 7.4; F, 21.5.

Anal. Calcd for $C_6H_{11}NF_2O_2$: C, 43.10; H, 6.63; N, 8.38; F, 22.73. Found: C, 42.82; H, 6.41; N, 8.69; F, 23.0.

γ-Difluoraminobutyryl Chloride and γ-Difluoraminobutyric Anhydride. - Thionyl chloride (40 g, 0.33 mol) was added dropwise, with stirring, to a solution of 42 g (0.30 mol) of γ-difluoraminobutyric acid in 220 ml of dry benzene. With a reflux condenser in place, the solution was heated at 60-65° for 45 min. Distillation gave 43 g (91 % yield) of γ-difluoraminobutyryl chloride, bp 29° (0.2 mm), n_D^{25} 1.4145.

Anal. Calcd for $C_4H_6NF_2ClO$: C, 30.50; H, 3.84; N, 8.89; F, 24.12. Found: C, 30.48; H, 3.82; N, 9.12; F, 24.0.

The proton nmr spectrum (CCl_4 solution) showed a quintet for $CH_2\underline{CH_2}CH_2$ at δ 2.53, a triplet of triplets (J_{HF} = 29 cps, J_{HH} = 8 cps) at δ 3.57 for $NF_2\underline{CH_2}CH_2$, and a triplet at δ 3.10 for $-\underline{CH_2}COCl$. The fluorine spectrum consisted of a triplet (J = 28 cps) at ϕ^* -54.6. The infrared spectrum showed carbonyl at 5.60 μ and bands in the NF region at 10.4 (s), 10.62 (m), 11.17 (m), 11.45 (s), and 11.92 μ (s).

A similar reaction using 15.3 g (0.11 mol) of γ-difluoraminobutyric acid and 12.0 g (0.10 mol) of thionyl chloride gave 9.0 g (57 % yield) of γ-difluoraminobutyryl chloride and 4.0 g (30 % yield) of γ-difluoraminobutyric anhydride, bp 105-106° (0.1 to 0.2 mm), n_D^{25} 1.4130.

Anal. Calcd for $C_8H_{12}N_2F_4O_3$: C, 36.93; H, 4.65; N, 10.77; F, 29.17. Found: C, 36.62; H, 4.56; N, 10 6; F, 30.5.

The infrared spectrum showed carbonyl bands at 5.50 and 5.71 μ.

γ-Difluoraminopropyl Isocyanate. - A stirred suspension of 13.7 g (0.21 mol) of recrystallized sodium azide in a solution of 31.5 g (0.20 mol) of γ-difluoraminobutyryl chloride in 360 ml of dry benzene was heated (using a reflux condenser) at 70-73° until nitrogen evolution ceased (50 min). The solution was filtered and distilled to give 23.0 g (85 % yield) of γ-difluoraminopropyl isocyanate, bp 66-67° (45 mm); n_D^{25} 1.4028.

Anal. Calcd for $C_4H_6F_2N_2O$: C, 35.30; H, 4.44; N, 20.58; F, 27.92. Found: C, 35.11; H, 4.40; N, 20.2; F, 27.9.

The fluorine nmr spectrum (CCl_4 solution) consisted of a triplet (J = 28 cps) at ϕ^* -55.2. The infrared spectrum showed NCO at 4.42 μ and bands in the NF region at 10.17, 10.98, 11.27, and 11.7 μ.

Ethyl N-(3-Difluoraminopropyl)carbamate. - A solution of 1.36 g (0.010 mol) of γ-difluoraminopropyl isocyanate in 10 ml of ethanol was allowed to stand at ambient temperature for 18 hrs. Distillation gave 1.64 g (90 % yield) of ethyl N-(3-difluoraminopropyl)carbamate, bp 66-67° (0.1 to 0.2 mm); n_D^{25} 1.4190.

Anal. Calcd for $C_6H_{12}N_2F_2O$: C, 39.56; H, 6.64; N, 15.38; F, 20.86. Found: C, 39.89; H, 6.51; N, 15.1; F, 21.2.

Fluorination of Cyclohexanecarboxamide. - A suspension of 12.7 g

(0.10 mol) of cyclohexanecarboxamide in 350 ml of acetonitrile was treated with 0.2 mol of fluorine at -15°. Half of the solution was stirred with solid sodium sulfate and distilled to give 1.1 g (18 % yield) of cyclohexyl isocyanate, bp 28-30° (0.1 mm), identified by spectral comparison with an authentic sample. The remaining acetonitrile solution was concentrated to 10 ml under vacuum and the residue was added to 100 ml of aqueous 10 % sodium bicarbonate. The aqueous phase was acidified and was extracted with 3-15 ml portions of methylene chloride. Removal of the solvent gave 3.1 g (48 % yield) of cyclohexanecarboxylic acid, identical with an authentic sample.

Fluorination of 0.1 mol of the amide in 350 ml of water (0-5°, 0.2 mol fluorine) gave, after extraction with hexane, 2.0 g (16 % conversion, 43 % yield) of cyclohexyl isocyanate and 8.0 g of the insoluble starting material.

Tetrafluorohydrazine. - A suspension of 23.6 g (0.40 mol) of acetamide in 250 ml of acetonitrile was fluorinated (0.8 mol of fluorine, 2 hrs, -10 to -20°). A 10 % aliquot of the resulting solution was added dropwise under a stream of helium to a stirred solution of 2.0 g of chromic anhydride in 40 ml of water at 5 to 7°. The reaction flask was connected, in series, to a 0° trap, a calcium sulfate drying tower, a -78° trap and a -195° trap. After 20 min, the final trap contained 0.010 mol (50 % yield by volumetric measurement) of tetrafluorohydrazine identified by its infrared spectrum.[17]

Acknowledgment. - The authors wish to thank Dr. H. M. Nelson and Mr. L. A. Maucieri for the nmr analysis and Mr. K. Inouye for the elemental analysis.

References

1. This work was supported by the Office of Naval Research and the Advanced Research Projects Agency.
2. V. Grakauskas and K. Baum, J. Am. Chem. Soc., 91, 1679 (1969).
3. V. Grakauskas and K. Baum, J. Org. Chem., in press.
4. R. E. Banks, R. N. Haszeldine and J. P. Lalu, J. Chem. Soc., C, 1966, 1514.
5. J. W. Frazer, J. Inorg. Nucl. Chem., 16, 63 (1960).
6. K. Baum, J. Am. Chem. Soc., 90, 7083 (1968).
7. V. Grakauskas, A. H. Remanick and K. Baum, J. Am. Chem. Soc., 90, 3839 (1968).
8. R. C. Petry and J. P. Freeman, J. Org. Chem., 32, 4034 (1967); F. A. Johnson, C. Haney and T. E. Stevens, J. Org. Chem., 32, 466 (1967); G. N. Sausen and A. L. Logothetis, ibid., 33, 2330 (1968); A. L. Logothetis and G. N. Sausen, ibid., 31, 3689 (1966); S. K. Brauman and M. E. Hill, J Am. Chem. Soc., 89, 2127 (1967); A. S. Filatov and M. A. Englin, Zh. Obshch. Khim., 38, 1408 (1968).
9. T. E. Stevens, J. Org. Chem., 31, 2025 (1966).
10. R. C. Petry and J. F. Freeman, J. Am. Chem. Soc., 83, 3912 (1961).
11. V. Grakauskas, U.S. Patent 3,350,172, October 31, 1967.
12. C. M. Sharts, J. Org. Chem., 33, 1008 (1968).
13. C. L. Coon, M. E. Hill and D. L. Ross, J. Org. Chem., 33, 1387 (1968).
14. V. Grakauskas, J. Org. Chem., 34, 963 (1969).
15. Allied Chemical Corp. Data Sheet PD-TA-85413A.
16. W. Reppe et al., Ann. Chem., 596, 93 (1955).
17. C. B. Colburn, Advan. Fluorine Chem., 3, 113 (1963).

APPENDIX C

Synthesis of α,α-Dinitro-N'-fluorodiimide N-Oxides[1]

Kurt Baum

Environmental Systems Division
Aerojet-General Corporation
Azusa, California 91702

Syntheses of N'-fluorodiimide N-oxides have been reported by reactions of tetrafluorohydrazine[2-6] or difluoramine[3,7] with nitroso compounds.

$$R\text{-}NO + HNF_2 \longrightarrow R\text{-}\overset{O}{\uparrow}N{=}NF + HF$$

$$R\text{-}NO + \cdot NF_2 \longrightarrow R\text{-}\overset{O}{\uparrow}N{=}NF + [F\cdot]$$

Pseudonitroles gave α-nitro-N'-fluorodiimide N-oxides[3,7], but α,α-dinitro-N'-fluorodiimide N-oxides have not been prepared directly; α,α-dinitro nitroso compounds are unknown.

In the present work, 1,1-dinitrobutyl-N'-fluorodiimide N-oxide was isolated from the reaction of the sodium salt of 1,1-dinitrobutane with tetrafluorohydrazine in methanol. The product was identified by analysis, and ir and nmr spectra. Most significantly, the F^{19} signal, -125 ppm from trifluoracetic acid, was in the region reported for other N'-fluorodiimide N-oxides. The mechanism

for this reaction may involve 1,1-dinitro-1-nitrosobutane as a transient intermediate. The nitrosating agent may be nitrous acid resulting from the Neff reaction of the starting material; 1,1-dinitrobutane was also formed. An acid source is the abstraction of hydrogen from the solvent to give difluoramine, which is readily dehydrofluorinated.

Preliminary work on this reaction was done with the salt of 1,1-dinitroethane, but the product was such a sensitive explosive that characterization could not be completed. The salt of nitroform did not react under these conditions. Sodium 2-propanenitronate on the other hand, yielded only the coupling product, 2,3-dimethyl-2,3-dinitrobutane, as reported by Freeman.[8]

Experimental Section

Caution. - Explosion shielding and remote manipulation are required for the N_2F_4 reaction and for product isolation.

1,1-Dinitrobutyl-N'-fluorodiimide N-oxide. - A Fischer-Porter aerosol tube containing a solution of 14.8 g (0.10 mol) of 1,1-dinitrobutane and 0.10 mol of sodium methoxide in 45 ml of methanol was evacuated at liquid nitrogen temperature and filled with nitrogen several times. The tube was charged with 0.2 mol of tetrafluorohydrazine and the mixture was stirred for 20 hrs at ambient temperature. The excess tetrafluorohydrazine was removed and most of the solvent was removed under vacuum. Methylene chloride (50 ml) was added and the solution was filtered and distilled to give 6.5 g of liquid, bp 46° (0.35 mm), which contained some 1,1-dinitrobutane. Chromatography with a 2 x 38 cm column of neutral active alumina and methylene chloride resulted in retention of the 1,1-dinitrobutane on the column as a bright yellow complex.

Distillation of the eluent gave 1.3 g (6.2% yield) of 1,1-dinitro-1-butyl-N'-fluorodiimide N-oxide, bp 34-35° (0.15 mm).

Anal. Calcd for $C_4H_7N_4FO_5$: C, 22.86; H, 3.33; N, 26.7; F, 9.05. Found: C, 23.20; H, 3.17; N, 26.63; F, 9.0.

The proton nmr spectrum consisted of a triplet (J = 8 Hz) at δ 1.12 for CH_3, a multiplet at δ 1.9 for $CH_3\underline{CH_2}$, and a triplet (J = 8 Hz) at δ 3.12 for the other methylene. The fluorine spectrum consisted of a broadened singlet at -125 ppm from external trifluoroacetic acid. The infrared spectrum consisted of bands at 3.42(m), 3.53(m), 6.4(vs), 6.9(m), 7.01(m), 7.3(m), 7.54(s), 9.05(w), 10.8(w), 11.7(m), 12.4(m), and 13.2 μ(m).

REFERENCES

1. This work was supported by the Office of Naval Research.

2. J. W. Frazer, B. E. Holder, and E. F. Worden, J. Inorg. Nucl. Chem., 24, 45 (1962).

3. T. E. Stevens and J. P. Freeman, J. Org. Chem., 29, 2279 (1964).

4. I. L. Knunyants, B. L. Dyatkin, and R. A. Becker, Dokl. Akad. Nauk SSSR, 170, 337 (1966).

5. A. N. Medvedev, K. N. Smirnov, S. S. Dubov, and V. A. Ginsburg, Zhur. Obshch. Khim., 38, 2462 (1968).

6. S. F. Reed, Jr., J. Org. Chem., 32, 3869 (1967).

7. K. Baum, J. Org. Chem., 34, 2049 (1969).

8. J. P. Freeman, Inorg. Chim. Acta Rev., 1, 65 (1967).

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) Environmental Systems Division Aerojet-General Corporation El Monte, California	2a REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b GROUP --

3 REPORT TITLE

RESEARCH IN NF COMPOUNDS

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Annual Report covering period 1 December 1968 through 1 December 1969

5 AUTHOR(S) (Last name, first name, initial)

Baum, K; Grakauskas, V.

6 REPORT DATE	7a TOTAL NO. OF PAGES	7b NO. OF REFS
January 1970	76	69

8a CONTRACT OR GRANT NO.	9a ORIGINATOR'S REPORT NUMBER(S)
N00014-69-C-0015 b PROJECT NO.	5015-2
c	9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d	

10 AVAILABILITY/LIMITATION NOTICES

Reproduction in whole or in part is permitted for any purpose of the United States Government.

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	The Office of Naval Research

13 ABSTRACT

Gem-diperchlorates were obtained by the reaction of ketones with anhydrous perchloric acid in halogenated solvents. Cyclohexene was reduced to cyclohexane by perchloric acid in chloroform.

Isopropyl chlorofluorocarbamate and bromofluorocarbamate added to olefins and acted as halogenating agents toward hydrocarbons by free radical chain mechanisms involving fluoraminocarboalkoxy free radicals. Isopropyl fluorocarbamate and mercuric oxide gave bis(carboisopropoxyfluoramino)mercury. The latter was found to add to olefins.

The following phases of earlier research were completed and the work was assembled in the form of manuscripts: (1) Direct Fluorination of Ureas, (2) Direct Fluorination of Amides, and (3) Synthesis of α,α'-Dinitro-N'-fluorodiimide N-Oxides.

alpha

DD FORM 1 JAN 64 1473 0101-807-6800

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Synthesis						
Nitrogen						
Fluorine						
IR spectra						
NMR spectra						
Nitro compounds						
Perchloric acid						
Free radicals						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

_____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

_____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through

_____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.