centrated by rotary evaporation and the products were determined by a comparison of infrared spectra of the collected peaks and vpc retention time with those of authentic samples. The amount of alcohols **9** and **10** was not sufficient to give infrared spectra of the desired intensity; the resulting spectra were very similar to, but not necessarily identical with, the spectra provided by Professor Closson.[13b] The identity of alcohol **11** was determined by oxidation with Jones reagent to the corresponding ketone and comparing the infrared spectra with that of spiro[2.4]heptan-5-one. The resolution of alcohols **6**, **7**, and **11** was poor by vpc until alcohol **11** was removed by oxidation. In order to determine the amount of alcohol **11** initially present in the solvolysis mixture, a comparison of the nmr integrals of the cyclopropyl protons and the exocyclic methylene protons of the complete solvolysis mixture was made. Since the amount of alcohol **8** and the amount of the alcohols, other than **11**, containing cyclopropyl rings were known the amount of alcohol **11** could be estimated. Repetitions of this study with ester concentrations of 0.02 *M* gave similar results.

A 33-mg portion of the *p*-toluenesulfonate ester **16** of spiro[2.4]-heptan-5-ol and 20 mg (100% excess) of sodium acetate were dissolved in 50 ml of acetic acid (prepared as above). The solution was kept under nitrogen and maintained at 75° for 35 hr. The solution was cooled, poured into 50 ml of water, and extracted with six portions of pentane. The pentane extracts were washed with a saturated solution of sodium bicarbonate and dried over anhydrous magnesium sulfate. The filtered solution was then concentrated by distilling the pentane through an 18-in. Vigreux column. About 100 ml of dry diethyl ether was added and the stirred solution was cooled in an ice bath. A 40-mg portion (10 equiv) of lithium aluminum hydride was added and the mixture was stirred for 2 hr at room temperature. The work-up was the same as for the solvolysis mixture above. The identities of the products were determined by vpc retention time. The identities of the two major products were confirmed by a comparison of the infrared spectra of the collected vpc peaks with those of authentic samples.

Procedure for Kinetic Runs. For each run the *p*-toluenesulfonate ester was about 0.001 *M* in acetic acid (reagent grade glacial acetic acid from Allied Chemical, distilled from 3% acetic anhydride, bp 117.0–117.8°). There was an 85–100% molar excess of anhydrous sodium acetate present for each run. The reaction was followed by the decrease in absorption at 272 mμ with time as recorded on a Beckman DU spectrometer. For the runs at 75°, aliquots were removed at timed intervals and stored until the completion of the run. The ultraviolet spectra were then recorded. For the runs at 45°, the solutions were placed directly in a spectrometer with a constant-temperature cell compartment maintained at 45°.

The Synthesis of Fluorammonium Salts[1]

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Abstract: The reaction of alkyl N-fluorocarbamates with sulfuric acid gave fluorammonium bisulfate, which was identified by nmr spectra and by reactions with cyclohexanone and *n*-butyraldehyde to give ε-caprolactam and *n*-butyronitrile, respectively. Fluorammonium perchlorate and fluorammonium methanesulfonate were isolated as pure salts from reactions of N-fluorocarbamates with perchloric acid and methanesulfonic acid, respectively. Ethyl N-fluoro-N-methylcarbamate and sulfuric acid gave methylfluorammonium bisulfate, which reacted with cyclohexanone to give N-methylcaprolactam. Nmr spectra of fluorammonium perchlorate indicated rapid hydrogen exchange in acetonitrile and ethyl acetate, but not in sulfuric acid.

Of the four possible fluorine-substituted ammonium ions, only the tetrafluoro derivative has been reported as a stable salt.[2,3] Difluoramine and trifluoramine have been reported to form reversible complexes with Lewis acids at low temperatures.[4] Fluoramine was claimed to be a by-product of the electrolysis of ammonium bifluoride[5,6] but the results have been shown to be in error.[7] Dimethylfluoramine was synthesized by the fluorination of unsymmetrical dimethylsulfamide and the compound was sufficiently basic to form a stable hydrochloride.[8] Fluorimmonium salts prepared by the rearrangement of alkyldifluoramines[9] can also be considered as alkylidene derivatives of substituted fluoramines.

Simple salts of fluoramine have now been prepared by the reaction of alkyl N-fluorocarbamates with strong acids. The starting materials are synthesized readily by the fluorination of alkyl carbamates.[10]

Fluorammonium Bisulfate. Fluorimmonium salts have been prepared and characterized in sulfuric acid. Under these conditions, the hydrolysis of N-fluorocarbamates in sulfuric acid would be expected to give the fluorammonium ion, which also should be stable.

When a solution of ethyl N-fluorocarbamate in concentrated sulfuric acid was heated at 85 to 90°, carbon dioxide and ethylene were evolved. The ^{19}F nmr spectrum of the sulfuric acid solution consisted of a quartet at 36.8 ppm relative to external trifluoroacetic acid, with a coupling constant of 38 cps. Thus, the fluorine was coupled to three equivalent hydrogens, and it is noteworthy that the hydrogens did not exchange rapidly with the solvent. By contrast, the ^{19}F spectrum of an unheated solution of ethyl N-fluorocarbamate in sulfuric acid consisted of a single broadened signal at 27.5 ppm; the NH protons of the starting material thus exchanged with the solvent rapidly by the nmr time scale.

Additional evidence for the fluorammonium ion structure was obtained from reactions with carbonyl compounds. The reaction of cyclohexanone with a sulfuric

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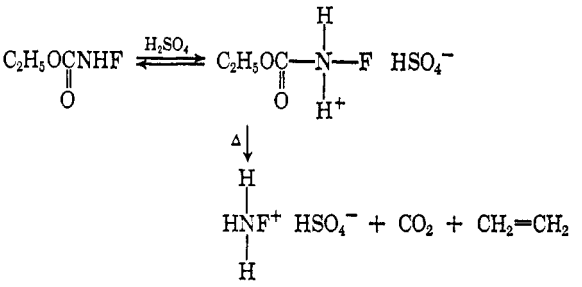
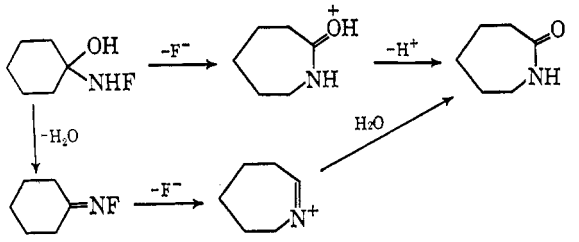


acid solution of fluorammonium bisulfate gave ϵ-caprolactam, isolated by quenching the mixture with ice. A probable intermediate was α-fluoraminocyclohexanol, which could lose a fluoride ion and undergo nucleophilic ring expansion. Alternatively, the dehydration of this alcohol could give fluoriminocyclohexane, which, in turn, would undergo a similar ring expansion. The Beckmann fragmentation of fluorimines has been reported recently.[11]



When *n*-butyraldehyde was treated similarly with the fluorammonium bisulfate solution, *n*-butyronitrile was formed. A related reaction, carried out in the presence of base instead of acid, is the synthesis of nitriles from aromatic aldehydes and chloramine.[12]

$$CH_3CH_2CH_2CHO \xrightarrow[H_2O]{NH_3F^+} CH_3CH_2CH_2C{\equiv}N$$

Attempts to isolate pure fluorammonium bisulfate, by diluting the sulfuric acid solution with organic solvents, were unsuccessful.

Fluorammonium Perchlorate. Perchloric acid, which is more volatile than sulfuric acid, appeared to offer better possibilities for the isolation of a pure fluorammonium salt. Accordingly, a solution of ethyl N-fluorocarbamate in 70% perchloric acid was heated until gas was evolved (68°), and the excess perchloric acid was then removed under vacuum. However, the product was contaminated by organic material of low volatility. Isopropyl N-fluorocarbamate reacted with 70% perchloric acid at a lower temperature than the ethyl ester (35 to 40°), and gave a less contaminated but still unsatisfactory product. Unexpectedly, fluorammonium perchlorate was found to have appreciable vapor pressure, subliming slowly at 46° (0.02 mm); the sublimed salt was analytically pure.

It is well recognized that the maximum 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.[13] Perchloric acid is soluble in chloroform;[14] therefore, this solvent, which has very low basicity, should enhance the acidity. Indeed, isopropyl N-fluorocarbamate reacted more rapidly with a 10% solution of anhydrous perchloric acid in chloroform than with the 70% commercial reagent. An additional advantage was that fluorammonium perchlorate was insoluble in chloroform. Analytically pure product was isolated directly in quantitative yield. The fate of the isopropyl group was not determined, but inasmuch as carbon dioxide free of propylene was liberated, it appears likely that isopropyl perchlorate was formed; if it was formed, it would remain in solution.[15]

$$(CH_3)_2CHOCNHF + 2HClO_4 \xrightarrow[42\text{–}43°]{CHCl_3} (CH_3)_2CHOClO_3 + CO_2\uparrow + \underline{NH_3FClO_4}$$

Fluorammonium perchlorate was a white solid which melted with decomposition at 104 to 105°. Differential thermal analysis showed a sharp exotherm at this temperature. The impact sensitivity was the same as that of RDX. The salt was hygroscopic and decomposed rapidly in the presence of atmospheric moisture. Although the synthesis and isolation were carried out in glass equipment under an atmosphere of dry nitrogen, some etching of the glass was visible after several hours of contact with the salt. However, samples have been stored at room temperature for several months, without decomposition, in fluorocarbon or passivated-nickel containers.

Fluorammonium perchlorate was insoluble in hydrocarbons and halocarbons; it was soluble in simple esters, nitriles, nitroalkanes, and in such ethers as monoglyme and tetrahydrofuran. It formed a 1:1 complex with dioxane. Concentrated solutions (*e.g.*, 30 to 50%) in any solvents were unstable, and in several instances fumed off shortly after they were prepared. Impure samples of the neat salt should also be handled with caution. Addition of chloroform to the ethyl acetate solution precipitated unchanged fluorammonium perchlorate.

The fluorine nmr spectrum of fluorammonium perchlorate in sulfuric acid consisted of a quartet (J = 44.1 cps) at 34.3 ppm from trifluoracetic acid (ϕ = 110.8), while the proton spectrum showed a doublet (J = 44 cps) at δ 10.28.[16] However, when acetonitrile was used as the nmr solvent, the proton spectrum gave a broadened singlet at δ 10.7, while the fluorine spectrum gave a slightly unsymmetrical singlet at ϕ 122.4. In ethyl acetate, the proton signal was a sharp singlet at δ 11.5, and the fluorine signal was a sharp singlet at ϕ 122.8. Thus, rapid hydrogen exchange took place in the organic solvents but not in sulfuric acid. If the mechanism of exchange were direct displacement of protons, a higher rate could be expected in sulfuric acid than in the organic solvents. The more basic solvents apparently allow dissociation of fluorammonium perchlorate, to a small extent, to fluoramine and perchloric acid. The high volatility of fluorammonium perchlorate compared to that of ammonium perchlorate might also be the result of dissociation.

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(16) One member of the doublet was obscured by the solvent signal in concentrated sulfuric acid, but was visible using 101% sulfuric acid.

$$H_3\overset{+}{N}F\ ClO_4^- \rightleftharpoons H_2NF + HClO_4$$

Fluorammonium Methanesulfonate. Fluorammonium methanesulfonate was synthesized by heating ethyl N-fluorocarbamate and methanesulfonic acid at 90°. The salt was precipitated by the addition of ether. The melting point and dta exotherm were essentially the same as those of the perchlorate and of the perchlorate–dioxane complex; this temperature range appears to be the stability limit of the fluorammonium ion. The infrared spectrum is described

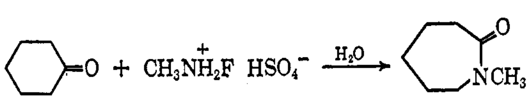
$$C_2H_5OC(=O)NHF + CH_3SO_3H \longrightarrow H_3NF^+\ CH_3SO_3^-$$

in the Experimental Section.

Methylfluorammonium Bisulfate. To determine whether substituted fluorammonium salts could be prepared by these methods, the reaction of ethyl N-fluoro-N-methylcarbamate with sulfuric acid was studied. Gas was evolved at 85 to 95°. The ^{19}F nmr spectrum of the sulfuric acid solution consisted of an incompletely resolved triplet of quartets at −29.5 ppm (external trifluoroacetic acid reference), with coupling constants of 42 cps to the NH_2 and 28 cps to the methyl.

$$FN(CH_3)CO_2C_2H_5 \xrightarrow[\Delta]{H_2SO_4} FNH_2CH_3^+\ HSO_4^-$$

A sulfuric acid solution prepared in this manner reacted with cyclohexanone and water to give N-methylcaprolactam.



These reactions are analogous to those of the unsubstituted fluorocarbamates and indicate broad applicability of the synthesis methods.

Experimental Section

Fluorammonium Bisulfate Solution. Ethyl N-fluorocarbamate (6.42 g, 0.060 mol) was added dropwise to 20 ml of concentrated sulfuric acid at room temperature, and the solution was heated at 85 to 90° until gas evolution ceased (20 min). A sample of the evolved gas was collected in an infrared cell and was shown by its spectrum to consist of carbon dioxide and ethylene. The 56.4-Mc ^{19}F nmr spectrum of the sulfuric acid solution consisted of a quartet at +36.8 ppm, referred to external trifluoroacetic acid, with J_{HF} = 38 cps. No ethyl N-fluorocarbamate remained. The ^{19}F spectrum of a 10% solution of ethyl N-fluorocarbamate in sulfuric acid, freshly prepared at room temperature, consisted of a single broadened signal at +27.5 ppm.

ε-Caprolactam. A fluorammonium bisulfate solution was prepared from 6.42 g (0.060 mol) of ethyl N-fluorocarbamate and 30 ml of concentrated sulfuric acid as above. To this solution at 0 to 2°, 4.9 g (0.050 mol) of cyclohexanone was added dropwise with stirring over a 25-min period. The resulting mixture was stirred at 5 to 10° for 30 min and was then poured onto 70 g of crushed ice. The mixture was neutralized with sodium hydroxide and extracted with five 50-ml portions of ether. The ether solution was dried over sodium sulfate and the solvent was distilled off. The residue was recrystallized from pentane to give 3.5 g (50% yield) of ε-caprolactam, mp 68° (not depressed in mixture melting point with an authentic sample).

***n*-Butyronitrile.** A solution of fluorammonium bisulfate prepared from 4.3 g (0.04 mol) of ethyl N-fluorocarbamate and 25 ml of concentrated sulfuric acid was added to a mixture of 80 g of crushed ice and 1.44 g (0.020 mol) of *n*-butyraldehyde. The mixture was allowed to stand for 18 hr at room temperature and was then extracted with four 30-ml portions of methylene chloride. The combined methylene chloride solutions were dried and distilled to give 1.1 g (76% yield) of *n*-butyronitrile, bp 118°. Its infrared spectrum was identical with that of an authentic sample.

Fluorammonium Perchlorate from Anhydrous Perchloric Acid. To a solution of 94 g (0.95 mol) of anhydrous perchloric acid[17] in 900 ml of chloroform (Baker's reagent grade, containing 0.6% methanol) was added dropwise at 24 to 28° a solution of 56.6 g (0.468 mol) of isopropyl N-fluorocarbamate in 40 ml of chloroform. The addition was conducted behind a safety barricade. The liberation of carbon dioxide (identified by ir) began immediately. The reaction mixture was heated at 42 to 43° until the gas evolution ceased (15 to 20 min) and was then cooled to 25°. The product was filtered under nitrogen, washed with five 100-ml portions of chloroform, and dried at 0.2 mm to give 63 g (0.465 mol, 99.5% yield) of fluorammonium perchlorate, mp 104–105° dec.

Anal. Calcd for NH_3ClFO_4: C, 0.0; H, 2.2; N, 10.4; F, 14.1. Found: C, 0.1; H, 2.3; N, 10.3; F, 14.0.

Fluorammonium Perchlorate from 70% Perchloric Acid. Isopropyl N-fluorocarbamate (2 g) was added dropwise with stirring at 25 to 30° to 2.8 g of 70% perchloric acid and the solution was heated for 1 hr at 35 to 40°. The solution was concentrated to half of its original volume at 40 to 43° (0.05 mm) and cooled to 20°. The product which precipitated was filtered under nitrogen and dried under vacuum to give 0.5 g of impure fluorammonium perchlorate.

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

A less pure product was obtained when the original reaction mixture was stripped to dryness.

When ethyl N-fluorocarbamate rather than the isopropyl derivative was used as the starting material, a reaction temperature of 68° was required, and product purity was affected adversely. Small samples of analytically pure fluorammonium perchlorate were isolated by subliming the crude material at 46° (0.02 mm). The addition of dioxane to a tetrahydrofuran solution of the crude product resulted in the precipitation of a 1:1 complex, mp 100–103° dec.

Anal. Calcd for $C_4H_{11}NClFO_6$: C, 21.5; H, 4.90; N, 6.6; F, 8.55. Found: C, 21.5; H, 5.06; N, 6.2; F, 8.2.

Fluorammonium Methanesulfonate. A solution of 1.5 g (0.014 mol) of ethyl N-fluorocarbamate in 6.2 ml of methanesulfonic acid was heated under nitrogen for 5 hr at 90 to 94°. The solution was cooled to room temperature, and ether was added until the mixture became cloudy. After 1 hr, the crystalline product was filtered under nitrogen, washed with ether, and dried under vacuum to give 1.05 g (57% yield) of white platelets, mp 103–105° dec.

Anal. Calcd for CH_6NSO_3F: C, 9.16; H, 4.57; N, 10.7; F, 14.5. Found: C, 9.33; H, 4.77; N, 10.8; F, 14.6.

The infrared spectrum of fluorammonium methanesulfonate obtained using Fluorolube (2–7.5 μ) and Nujol (7.5–16 μ) mulls consisted of peaks at 3.0 (sh), 3.20 (m), 3.30 (m), 3.58 (w), 6.2–6.6 (w), 7.15 (m), 7.50 (w), 8.05 (sh), 8.2–9.6 (s), 9.44 (s), 9.69 (s), 12.4 (sh), 12.67 (m), 12.90 (w), 13.9 (w), and 14.7 μ (w).

The ^{19}F nmr spectrum in sulfuric acid was identical with that of the bisulfate solution.

Methylfluorammonium Bisulfate Solution. A solution of 6.0 g (0.050 mol) of ethyl N-fluoro-N-methylcarbamate in 20 ml of concentrated sulfuric acid was heated at 85 to 95° until gas evolution ceased (20 min). The ^{19}F nmr spectrum of this solution consisted of an incompletely resolved triplet of quartets at −29.5 ppm (external trifluoroacetic acid reference), J_{NH_2-F} = 42 cps and J_{CH_3-F} = 28 cps.

N-Methylcaprolactam. A methylfluorammonium bisulfate solution prepared from 6.1 g (0.05 mol) of ethyl N-fluoro-N-methylcarbamate and 30 ml of sulfuric acid was cooled to 0° and added to a mixture of 150 g of crushed ice and 4.4 g (0.045 mol) of cyclohexanone. The resulting solution was allowed to stand at room temperature for 4 hr, and then was extracted with four 25-ml portions of methylene chloride. The combined methylene chloride solutions were dried with Drierite and distilled to give 2.5 g (44% yield) of N-methylcaprolactam, bp 50° (0.3 mm), $n^{25}D$ 1.4814 (lit.[18] bp 20° (19 mm), $n^{25}D$ 1.4818).

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