This reaction also shows the greatest rate acceleration (relative to identical supercooled solutions at the same temperature) that has so far been observed for a frozen state reaction. At the lowest concentration studied (0.001 *M* reactants), while the frozen system at −5.0° is 99.9% solid, the reaction is accelerated by a factor of 1000. Although there is a tendency to loosely describe all frozen systems as solid, it is apparent that as far as the ethylene chlorohydrin is concerned, the important part of the system studied here is the normal (but concentrated) liquid which makes up only *ca.* 0.1% of the total volume.

Experimental Section

Materials. Ethylene chlorohydrin (2-chloroethanol, Eastman Organic Chemicals) was distilled through a 75-cm Vigreux column. After discarding a large forerun, a center fraction with bp 128.5–130° was collected. Deionized water was boiled to remove carbon dioxide and stored in a flask protected with an Ascarite tube. For runs at the lowest concentrations (0.001 *M*), the water used was distilled from acidic permanganate and then from barium hydroxide.

Sodium hydroxide solutions were made up from British Drug Houses concentrated volumetric solutions or by dissolving U.S.P. grade pellets. These solutions were standarized against potassium acid phthalate. Reagent grade sodium chloride and sodium nitrate were dried at 110° for 2 hr before using. Absolute ethanol was refluxed with and distilled from anhydrous calcium oxide.

Kinetic Studies. Ethylene chlorohydrin solutions were made up fresh each day by weighing out the material and diluting with water. The required amount of this solution was mixed with the appropriate volume of sodium hydroxide solution and then diluted with water to give the concentration desired for a run. After thorough mixing, the solution was divided into several vials. Freezing of these individual samples of a run was usually accomplished simply by placing the samples in a Dry Ice–acetone bath. Sometimes the samples were supercooled to the temperature of a run and then dipped quickly into a Dry Ice–acetone bath to initiate crystallization.

At various times, individual samples were removed from the constant temperature bath and quickly thawed by shaking under hot tap water. Analysis of the samples was carried out by titration with standard hydrochloric acid solution (usually 0.05 *M*) with phenolphthalein as indicator. Microburets of 5- and 2-ml capacity were used, the 2-ml buret being equipped with a micrometer plunger. For runs at low concentrations of base pH measurements on individual thawed samples were made using a Radiometer Model 4 pH meter which was standardized against pH 10 buffer. No correction was made for the deviation of the activity coefficient from unity. For example, a run with 0.001 *M* reactants gave the following pH readings at the given times: 10.967 at 0 min, 10.848 at 46 min, 10.718 at 99 min, 10.681 at 150 min, 10.698 at 188 min, 10.632 at 239 min, 10.493 at 409 min, and 10.385 at 607 min.

Kinetic data were treated according to normal second-order kinetic equations. Rate constants were calculated from the slopes of the lines in plots of reciprocal concentration against time or plots of log $[ClCH_2CH_2OH]/[OH^-]$ against time. Runs at the lowest concentration showed some scatter (see Figure 1). This seemed due to experimental difficulties in measuring low concentrations of base rather than to real variations in the amount reacted. As indicated by changes in pH, this reaction in frozen solutions proceeds even with initial concentrations less than 10^{-3} *M*, but individual thawed samples gave very erratic pH readings at these low concentrations of base.

The value of C_h was obtained by measuring the freezing point of aqueous solutions containing various concentrations of ethylene chlorohydrin. The concentration–temperature relationship down to −10° was the same as reported for ethanol in water.[18] In terms of decrease in freezing point per mole of solute, sodium chloride and sodium hydroxide differ little from either ethanol or ethylene chlorohydrin in the temperature range of interest (down to *ca.* −10°).[19]

The values of k_2 at 1° intervals were calculated (IBM 7040 computer) from the equation[12] k_2 (l. mole^{-1} sec^{-1}) = $10^{16.8}/60e^{-23,300/RT}$. Runs using supercooled liquid samples showed that our method of analysis gave rate constants in agreement with McCabe and Warner[12] (at −1.4° found, 2.06×10^{-4} l. mole^{-1} sec^{-1}; at −1.0°, calculated 2.04×10^{-4} l. mole^{-1} sec^{-1}).

(18) "Handbook of Chemistry and Physics," 46th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p D-135.
(19) Reference 18, pp D-158, D-159.

Reactions of Alkyldifluoramines with Acids[1]

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Abstract: The reaction of *t*-butyldifluoramine with boron trifluoride gave the stable salt, N-fluoro-N-methylisopropylidenimonium fluoroborate. This rearrangement also occurred in the reaction of *t*-butyldifluoramine with sulfuric acid, and the above cation was identified by nmr spectra of the resulting solution. Ethyldifluoramine reacted with sulfuric acid to give acetonitrile, which was hydrated under the experimental conditions to give acetamide. 1-Difluoraminobutane and 2-difluoraminobutane reacted with sulfuric acid, and nmr spectra indicated that the products were the N-fluorimonium ions resulting from migration of the propyl and ethyl groups, respectively.

The reaction of triphenylmethyldifluoramine with concentrated sulfuric acid has been reported by Graham and Parker[2] to give difluoramine and triphenylmethyl cation.

$$(C_6H_5)_3CNF_2 \xrightarrow{H_2SO_4} (C_6H_5)_3C^{\oplus} + HNF_2$$

Thus, the difluoramino entity functions as a leaving group under the driving force of the formation of the highly stable trityl cation. It was of interest to determine whether this type of cleavage would occur in the reaction of acids with other difluoramino derivatives, not capable of producing such a highly stabilized carbonium ion.

(1) Supported by the Office of Naval Research and the Advanced Research Projects Agency. Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, and the Third International Fluorine Symposium, Munich, Sept 1965.
(2) W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963).

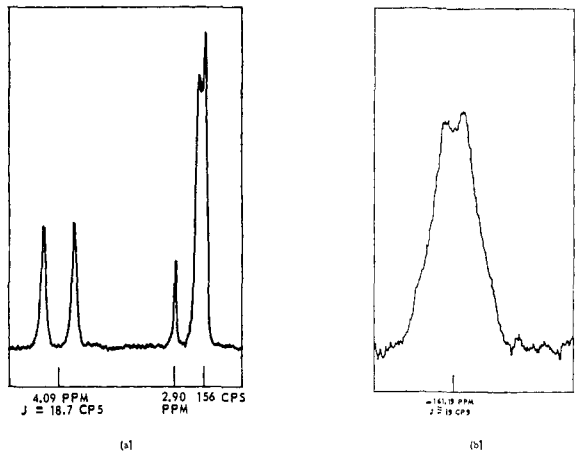


Figure 1. Nmr spectra of *t*-butyldifluoramine product: (a) proton, (b) fluorine.

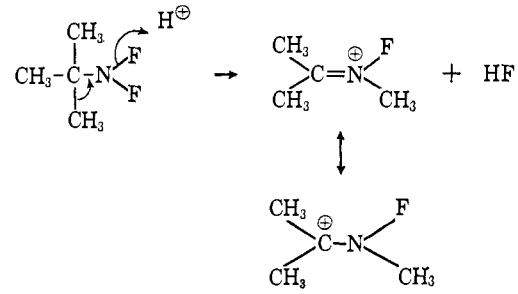
Reactions of acids with the three isomeric difluoraminobutanes and with ethyldifluoramine were studied in the present work. The synthesis of *t*-butyldifluoramine has been reported by Petry and Freeman[3] by the reaction of azoisobutane with tetrafluorohydrazine. Bumgardner[4] reported the preparation of 1-difluoraminobutane and 2-difluoraminobutane by the reaction of butane with tetrafluorohydrazine. Frazer[5] reported the synthesis of ethyldifluoramine from ethyl iodide and tetrafluorohydrazine.

***t*-Butyldifluoramine.** The reaction of *t*-butyldifluoramine with concentrated sulfuric acid was first examined by introducing a sample of this N–F compound into an evacuated glass bulb containing sulfuric acid. The pressure in the bulb began to decrease immediately and was reduced to 8% of the molar theoretical value in 4 hr and to 5% in 2 days. The infrared spectrum of the remaining gas showed that it was mainly silicon tetrafluoride, and that no difluoramine was present.

The nature of the product soluble in sulfuric acid was examined by nuclear magnetic resonance spectroscopy. A fresh solution for this purpose was prepared by shaking liquid *t*-butyldifluoramine and sulfuric acid at 0° until a clear solution was formed. The proton nmr spectrum at 60 Mc (Figure 1a) consisted of a doublet at 4.09 ppm (referred to tetramethylsilane[6]) with a coupling constant of 18.7 cps, a complex multiplet with maximum intensity at 156 cps, and a small singlet at 2.90 ppm which increased with time. The position of the singlet was identical with that of a solution of acetone in sulfuric acid, indicating that acetone was a decomposition product of the initial product. The 56.4-Mc F^{19} nmr spectrum (Figure 1b) of the sulfuric acid solution was recorded using trifluoroacetic acid as an external reference. The spectrum consisted of a partially resolved quartet at −141.57 ppm with splitting of approximately 15 cps, and a singlet at −116.8 ppm. The latter resonance was assigned to HF; its position was identical with that of a solution of HF in sulfuric acid.

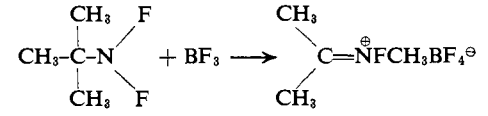
(3) R. C. Petry and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 3912 (1961).
(4) C. L. Bumgardner, *Tetrahedron Letters*, **48**, 3683 (1964).
(5) J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 65 (1960).
(6) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

The observed nmr peaks are those which would be expected for the N-fluoro-N-methylisopropylidenimonium ion, the product of methyl migration to the nitrogen with fluoride as the leaving group. Thus, the F^{19} spectrum indicates coupling of a fluorine to three protons. The proton doublet at 4.09 ppm is assignable to the N-methyl group and the 156-cps multiplet to the C-methyls.



If the cation had a large carbonium ion contribution, free rotation would average the chemical shifts of the C-methyls. The C-methyl signal would then be broadened only by a relatively small homoallylic coupling to the N-methyl protons and possibly by allylic coupling to the fluorine. Neither of these couplings nor a combination would produce the observed asymmetric multiplet, which is broad compared to the components of the N-methyl doublet. It must be concluded that rotation is slow compared to the unknown but probably small difference in chemical shift of the C-methyls.

This rearrangement was also affected by a Lewis acid. When a mixture of boron trifluoride and nitrogen was bubbled through a solution of *t*-butyldifluoramine in pentane at −78°, a 59.5% yield of analytically pure N-fluoro-N-methylisopropylidenimonium fluoroborate was isolated. The reaction of *t*-butyldifluoramine with boron trifluoride was also carried out in the absence of solvent at −78°.



The proton nmr spectrum of the fluoroborate (Figure 2a), using concentrated sulfuric acid as the solvent, was similar to that of the solution that was prepared by treating *t*-butyldifluoramine with concentrated sulfuric acid, but had better resolution. Fine structure, apparently due to homoallylic coupling to the C-methyls, is evident in the components of the N-methyl doublet. The signal assigned to the C-methyls also shows additional splitting. The F^{19} nmr spectrum of the fluoroborate (Figure 2b) consisted of a quartet at −140.94 ppm, with a coupling constant of 18.5 cps, and singlets at −116.9 and +67.5 ppm. The position of the quartet is within experimental error of that of the sulfuric acid catalyzed rearrangement product of *t*-butyldifluoramine. The latter two peaks were also found in the F^{19} spectrum of a solution prepared by adding commercial aqueous fluoroboric acid to concentrated sulfuric acid. The −116.9-ppm band corresponds to HF but the +67.5-ppm band is shifted somewhat from that of a solution of BF_3 in sulfuric

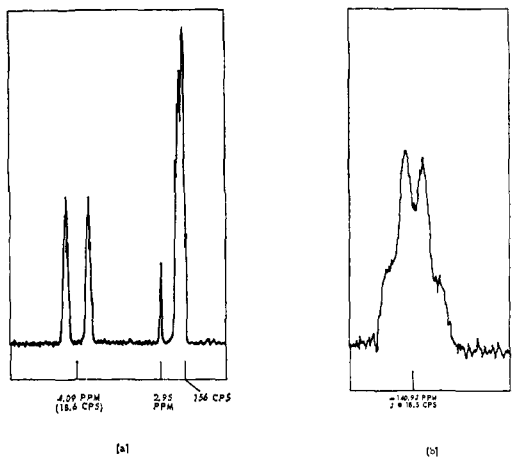


Figure 2. Nmr spectra of N-fluoro-N-methylisopropylidenimonium fluoroborate: (a) proton, (b) fluorine.

tion of HF to form acetonitrile, which undergoes hydration to acetamide under the experimental conditions.

$$CH_3CH_2NF_2 \xrightarrow{-HF} CH_3CN \longrightarrow CH_3CONH_2$$

1-Difluoraminobutane. The reaction of 1-difluoraminobutane with sulfuric acid did not follow the same course as that of ethyldifluoramine. The nmr spectra of the solution formed by shaking 1-difluoraminobutane with sulfuric acid were consistent with the propyl migration product, N-fluoro-N-propylmethylenimonium ion.

$$CH_3CH_2CH_2CH_2NF_2 \longrightarrow \left[\begin{array}{c} H \quad F \\ \diagdown \; \diagup \\ C{=}N^{\oplus} \\ \diagup \; \diagdown \\ H \quad CH_2CH_2CH_3 \end{array}\right]$$

The proton nmr spectrum of the sulfuric acid solution is shown in Figure 3a. The low-field group of signals

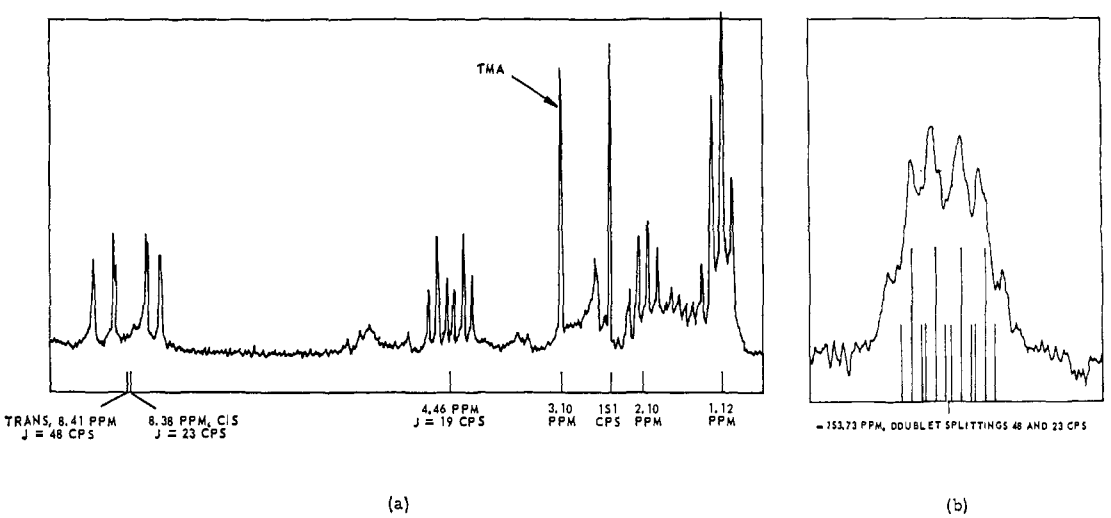


Figure 3. Nmr spectra of 1-difluoroaminobutane product: (a) proton, (b) fluorine.

acid (+65.82 ppm). The equilibrium of HBF_4 with HF and BF_3 is well known in aqueous solutions.[7]

The fluoroborate was extremely hygroscopic and decomposed rapidly when it was exposed to the atmosphere. It did not change, however, under prolonged storage under dry nitrogen at room temperature. The addition of the salt to water gave acetone which was isolated at its 2,4-dinitrophenylhydrazone.

Ethyldifluoramine. Ethyldifluoramine was less reactive toward concentrated sulfuric acid than the *t*-butyl derivative was, but a homogeneous solution was formed when the mixture was shaken at room temperature. The proton nmr spectrum of this solution consisted of two sharp singlets at 2.51 and 2.22 ppm. After 48 hr, the spectrum of the same sample showed only the 2.51-ppm signal and a very broad, weak signal at 8.5 ± 0.2 ppm. The proton spectrum of acetonitrile in sulfuric acid exhibited the identical behavior; the 2.22-ppm signal disappeared in 2.5 hr. A solution of acetamide in sulfuric acid gave a sharp singlet at 2.51 ppm and a broad peak at 8.3 ± 0.2 ppm. The reaction of ethyldifluoramine with sulfuric acid thus results in elimination of HF to form acetonitrile, which undergoes hydration to acetamide under the experimental conditions.

$$CH_3CH_2NF_2 \xrightarrow{-HF} CH_3CN \longrightarrow CH_3CONH_2$$

1-Difluoraminobutane. The reaction of 1-difluoraminobutane with sulfuric acid did not follow the same course as that of ethyldifluoramine. The nmr spectra of the solution formed by shaking 1-difluoraminobutane with sulfuric acid were consistent with the propyl migration product, N-fluoro-N-propylmethylenimonium ion.

$$CH_3CH_2CH_2CH_2NF_2 \longrightarrow \left[\begin{array}{c} H \quad F \\ \diagdown \; \diagup \\ C{=}N^{\oplus} \\ \diagup \; \diagdown \\ H \quad CH_2CH_2CH_3 \end{array}\right]$$

The proton nmr spectrum of the sulfuric acid solution is shown in Figure 3a. The low-field group of signals is assignable to the methylene protons. The inner two members are seen to be doublets, while the outer ones are broadened. It seems reasonable to assign the outer signals to the proton *trans* to fluorine (8.41 ppm, J = 48 cps) and the inner pair to the proton *cis* to fluorine (8.38 ppm, J = 23 cps). The additional splitting of the components of the later doublet is attributed to geminal coupling to the *trans* proton. The signals at 4.46, 2.10, and 1.12 ppm are assignable to the propyl group: the pair (19 cps) of triplets at 4.46 ppm to the α-methylene, the sextet at 2.10 ppm to the β-methylene, and the triplet at 1.12 ppm to the methyl. The singlet at 151 cps and other weaker signals are apparently the result of impurities.

The doublet splitting of the *trans* proton signal is apparently obscured by an additional allylic coupling to the α-methylene protons of the propyl group. The olefinic protons represent, in fact, the AB portion of an ABX spectrum.[8] The fluorine, or X, portion is additionally complicated by a 19-cps coupling to the propyl α-methylene protons.

Since $|J_{AX} + J_{BX}|$ must correspond to the separation

(7) A. V. Topchiev, S. V. Savgorodnii, and Y. M. Panshkin, "Boron Fluoride and Its Compounds as Catalysts in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 56.

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 132–138.

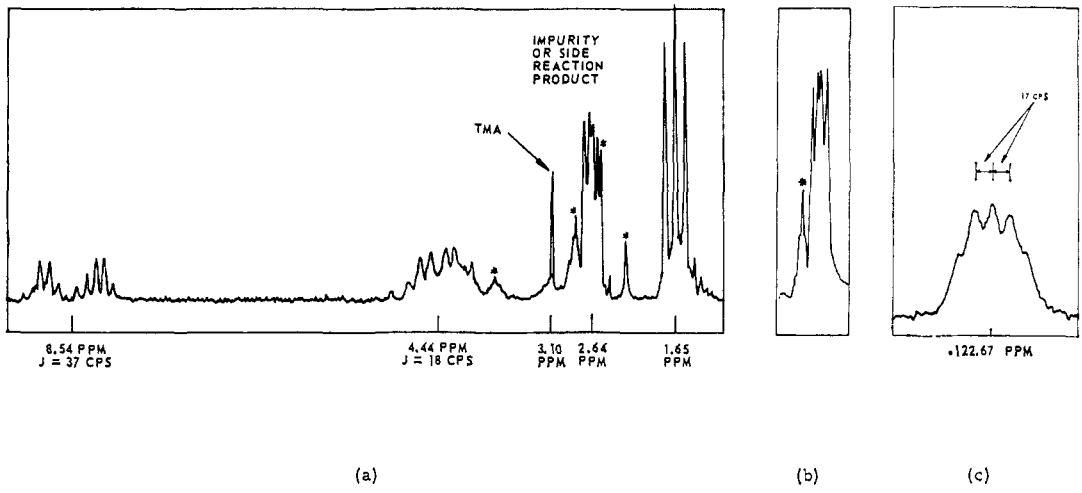


Figure 4. Nmr spectra of 2-difluoraminobutane product: (a) proton, (b) 2.6-ppm region of proton spectrum shortly after mixing, (c) fluorine.

of the strongest pair of lines in the X spectrum (either 25 or 71 cps, see Figure 3b) the alternative choices for the two AB quartets are narrowed to four. These produce the following sets of coupling constants (cps): (1) ±33, ±37; (2) ±23, ±48; (3) ±11, ±14; (4) ±23, ±48. Set 1 makes the *cis* and *trans* couplings too similar, while set 3 makes them too small. Sets 2 and 4 give the couplings an appropriate ratio and magnitude, but only set 2 is consistent with the analogous observed couplings in 2-fluoropropene[9] (+48.6 and 16.6 cps). Thus, it appears that set 2 is the correct choice and that the intensities in the fluorine spectrum are distorted by the relatively poor resolution and/or the additional triplet splitting. In either case we have

$$J_{AB}^2 \ll \left[\nu_A - \nu_B \pm \frac{1}{2}(J_{AX} - J_{BX})\right]^2$$

so that

$$D_{\pm} = \frac{1}{2}\left[\nu_A - \nu_B \pm \frac{1}{2}(J_{AX} - J_{BX})\right]$$

This circumstance causes the means of the transitions to correspond to chemical shifts and their separations to coupling constants so that the first-order interpretation given is justified.

The F^{19} spectrum is given in Figure 3b. An HF signal was observed at −116.55 ppm but is not shown in the figure. On the basis of the assignments made for the proton spectrum this signal is expected to be a doublet (48 cps) of doublets (23 cps) of triplets (19 cps). The observed and predicted spectra are compared in Figure 3b. The predicted separation of the inner four members of the multiplet are 23, 25, and 23 cps. The observed separations are 21, 25, and 21 cps.

2-Difluoraminobutane. The rearrangement of 2-difluoraminobutane with sulfuric acid could be envisioned as taking place by methyl migration to give N-fluoro-N-methylpropylidenimonium ion

$$CH_3CHNF_2CH_2CH_3 \longrightarrow CH_3\overset{\oplus}{N}F{=}CHCH_2CH_3$$

(9) M. Y. DeWolf and J. D. Baldeschwieler, *J. Mol. Spectry.*, **13**, 344 (1964).

or by ethyl migration to give N-fluoro-N-ethylethylidenimonium ion.

$$CH_3CHNF_2CH_2CH_3 \longrightarrow CH_3CH_2\overset{\oplus}{N}F{=}CHCH_3$$

The nmr spectra of a solution prepared by shaking 2-difluoraminobutane with sulfuric acid support the latter reaction product.

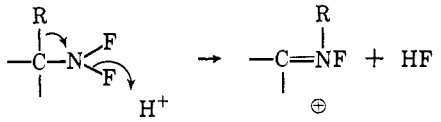
In the proton spectrum (Figure 4a) the pair (37 cps) of quartets at 8.54 ppm is attributed to the $CH_3CH{=}$ proton. The ethyl group signal consists of a pair (18 cps) of quartets at 4.44 ppm and a triplet at 1.65 ppm. The signal of the remaining methyl group in Figure 4a is obscured by decomposition products in the 2.5–3.1-ppm region. By recording rapidly this portion of the spectrum using a freshly prepared sample, the curve in Figure 4b was obtained, showing a pair of doublets centered on 2.64 ppm. Quickly, however, an additional signal appeared on the high-field side of the multiplet and the central region of the multiplet itself became distorted. Acetaldehyde, the expected hydrolysis product of the ion, was not the source of the interference, since it gave a doublet at 2.87 ppm in sulfuric acid. Acetaldehyde, however, underwent a rapid self-condensation to crotonaldehyde under these conditions, giving a doublet at 2.57 ppm, the position of the interference.

If the rearrangement product is assumed to consist of a single noninterconverting *cis* or *trans* isomer, the additional splitting of the methyl group may be attributed to an allylic coupling to fluorine. The magnitude of the doublet splitting of the olefinic signal would indicate that the product is the *trans* isomer. The additional weak signals in the olefinic region may then be attributed to the presence of a relatively small amount of the *cis* isomer.[10]

(10) As an alternative to the long-range coupling to fluorine, an intermediate rate of internal rotation may be invoked to explain the additional methyl group splitting. The 37-cps splitting of the olefinic hydrogen is not greatly different from the average of the *cis* and *trans* splittings in the 1-difluoramino product. The difference in chemical shift for *cis* and *trans* protons would be expected to be small by analogy to the observed 0.03-ppm difference in the 1-difluoraminobutane product. Thus, a low rate of rotation might be sufficient to average this small difference, but not a larger difference for the *cis* and *trans* C-methyls which would appear as two doublets. This explanation, however, is difficult to reconcile with the lack of evidence for rotation for the other N-fluorimonium ions.

On the basis of the assignments in the proton spectrum, the -NF- fluorine signal should appear as an overlapping pair (37 cps) of triplets (18 cps). Allylic coupling to methyl would produce an additional and probably unresolvable splitting of each of the components into quartets. While the resolution is relatively poor the observed 17-cps separation (Figure 4c) is in good agreement with that expected. In addition, a sharp singlet attributable to HF appears at −116.79 ppm.

Mechanism. The rearrangement of alkyldifluoramines to N-fluorimonium ions can be rationalized as a nucleophilic alkyl migration with fluoride leaving.



In the absence of kinetic data one cannot be certain whether the loss of fluoride is concerted with the alkyl migration. A concerted mechanism, however, appears probable in view of the preponderance of evidence for this type of path in rearrangements to electron-deficient nitrogen.[11] Information about the nature of the transition state might be obtained by comparing the observed migratory aptitudes with those reported for related rearrangements. The most closely related rearrangement to nitrogen for which analogous examples have been reported is the Schmidt rearrangement of alkyl azides, although it involves a ground-state species containing a full positive charge, the conjugate acid of the azide. Triphenylmethyl azide and simple *t*-alkyl azides give reactions with sulfuric acid parallel to those of the corresponding difluoramine derivatives, ionization to trityl cation and hydrazoic acid for the former,[12a] and alkyl migration to nitrogen for the latter.[12b] Primary alkyl azides, on the other hand, show an increased tendency toward hydrogen migration rather than alkyl group migration as the chain length is increased.[13]

The examples in the present study are characterized by the failure of methyl groups to migrate when another group is available. This behavior is reminiscent of the Baeyer–Villiger rearrangement, and has been rationalized on the basis of a transition state in which positive charge resides on the migrating group.[14]

Experimental Section

Nuclear Magnetic Resonance Spectra. The spectra were obtained using a Varian Associates DP-60 instrument equipped with a V 3521 A integrator/decoupler. Probe balance and base-line stability were considerably improved by interchanging the positions of the coarse paddles. Spectra were calibrated by the usual audio side band technique. Internal tetramethylammonium ion (TMA) was used as a reference for the proton spectra. Signal positions are given in ppm or cps from internal tetramethylsilane (TMS) based on a difference of 3.10 ppm between TMA and TMS in 96% H_2SO_4.[6] Fluorine signal positions are referred to external trifluoroacetic acid (TFA) positive upfield.

Reaction of Alkyldifluoramines with Sulfuric Acid. A stoppered test tube containing 1 ml of concentrated sulfuric acid was cooled in an ice bath and 0.2 ml of the alkyldifluoramine was added. The test tube was agitated with a Vortex mixer with intermittent cooling in an ice bath, until a clear solution was formed. Solutions prepared in this manner were used for nmr measurements.

The reaction of sulfuric acid with *t*-butyldifluoramine was initially studied with the latter reagent in the gas phase. A 500-ml, three-necked flask (550-ml measured capacity) was fitted with a manometer, a vacuum system adaptor, and a break-tip ampoule containing 1.0 g (10.5 mmoles) of *t*-butyldifluoramine. Concentrated sulfuric acid (50 ml) was introduced and the flask was evacuated. The *t*-butyldifluoramine was released into the closed system. After 4 hr, the pressure in the bulb was 29 mm (8% of theoretical for a perfect gas) and after 2 days the pressure was 18 mm (5% of theoretical). The infrared spectrum of this gas indicated that it was silicon tetrafluoride.

N-Fluoro-N-methylisopropylidenimonium Fluoroborate. A solution of 3.0 g (27.5 mmoles) of *t*-butyldifluoramine in 15 ml of pentane was placed in a three-necked, 50-ml flask fitted with a gas inlet, a magnetic stirrer, and a drying tube containing Drierite. The flask was cooled in a −78° bath and an approximately equal mixture of boron trifluoride and nitrogen was bubbled through the stirred solution until no further precipitation of solid took place. The white solid was filtered in a drybox under nitrogen and was dried under vacuum to give 2.90 g (16.4 mmoles, 59.5% yield) of N-fluoro-N-methylisopropylidenimonium fluoroborate, mp 134–138° dec.

Anal. Calcd for $C_4H_9NBF_5$: C, 27.11; H, 5.08; N, 7.91; F, 53.8. Found: C, 26.90; H, 5.22; N, 7.80; F, 51.9.

This reaction was also conducted by passing a mixture of boron trifluoride and nitrogen over 3.0 g (27.5 mmoles) of undiluted *t*-butyldifluoramine at −78°. After the product was allowed to warm to room temperature under a rapid stream of nitrogen, 1.5 g (8.5 mmoles, 31% yield) of the fluoroborate was isolated. The reduced yield was probably the result of physical separation of unreacted *t*-butyldifluoramine from the boron trifluoride by the initially formed fluoroborate. The unreacted starting material would be swept out by the nitrogen stream at room temperature. Despite the lower yield, this method is more convenient for the preparation of small quantities of the fluoroborate.

N-Fluoro-N-methylisopropylidenimonium fluoroborate was stable at room temperature, and underwent no noticeable decomposition during storage for several months under dry nitrogen. The material reacted very rapidly, however, with atmospheric moisture. A small sample of the fluoroborate was added to water and a vigorous reaction resulted. The infrared spectrum of the methylene chloride extract of the aqueous solution showed acetone was formed. Acetone 2,4-dinitrophenylhydrazone, mp 126°, was isolated in 50% yield when the standard reagent[15] (from 0.4 g of 2,4-dinitrophenylhydrazine, 2 ml of concentrated sulfuric acid, 3 ml of water, and 10 ml of 95% ethanol) was added to the solution formed by adding 0.40 g of the fluoroborate to 20 ml of ethanol.

Acknowledgment. The authors are indebted to Mr. F. J. Gerhart for assistance in the synthesis work, to Mr. K. Inouye for elemental analysis, and to Dr. David G. Adams of the U. S. Rubber Company Research Center for a helpful discussion of the nmr interpretations.

(11) P. A. S. Smith, "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 457–592.

(12) (a) M. M. Coombs, *J. Chem. Soc.*, 4200 (1958); (b) C. Schuerch and E. H. Huntress, *J. Am. Chem. Soc.*, 71, 2238 (1949); German Patent 583,565 (1935).

(13) K. W. Sherk, A. G. Houpt, and A. W. Browne, *J. Am. Chem. Soc.*, **62**, 329 (1940); J. H. Boyer, F. C. Canter, J. Hamer, and R. L. Putney, *ibid.*, 77, 3287 (1955).

(14) J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

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