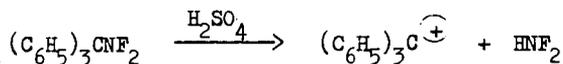


The Formation of N-Isopropylidene-N-fluoro-N-methylammonium
Ion from *t*-Butyldifluoramine

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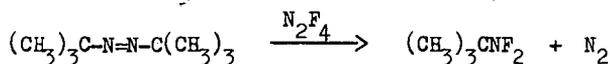
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The reaction of triphenylmethyldifluoramine with concentrated sulfuric acid has been reported by Graham and Parker¹ to give difluoramine and triphenylmethyl cation.



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 another difluoramine derivative that is not capable of producing such a highly stabilized carbonium ion. The compound might be inert or it might undergo an alternative mode of degradation.

Reactions of *t*-butyldifluoramine with acids were studied in the present work. The synthesis of this compound has been reported by Petry and Freeman² by the reaction of azoisobutane with tetrafluorohydrazine:

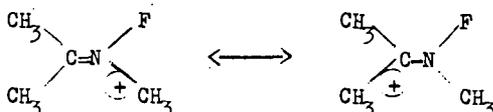


The reaction of *t*-butyldifluoramine with concentrated sulfuric acid was first examined by introducing a sample of this N-F compound into an evacuated glass bulb containing sulfuric acid. The pressure in the bulb began to decrease immediately, and was reduced to 8% of the molar theoretical value in four hours and to 5% in two days. The infrared spectrum of the remaining gas showed that it was mainly silicon tetrafluoride, and that no difluoramine was present. Thus, this reaction is not analogous to that of trityldifluoramine with sulfuric acid. A product soluble in sulfuric acid was formed.

The nature of this product was examined by nuclear magnetic resonance spectroscopy. A fresh solution was prepared by shaking a mixture of *t*-butyldifluoramine and sulfuric acid in a stoppered test tube. A clear solution was formed in about ten minutes. The proton NMR spectrum³ at 60 m.c. consisted of a doublet at 4.09 p.p.m. with a coupling constant of 18.7 c.p.s., a complex multiplet at 156 c.p.s. and a small singlet at 2.90 p.p.m. 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.

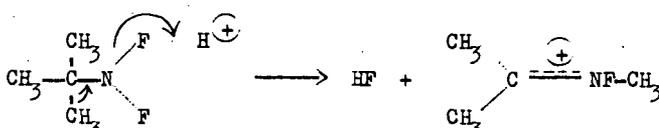
The 56.4 m.c. F^{19} NMR spectrum of the sulfuric acid solution was recorded using trifluoroacetic acid as an external standard. The spectrum consisted of a partially resolved quartet at -141.57 p.p.m. with splitting of approximately 15 c.p.s., and a singlet at -116.8 p.p.m. The latter resonance was assigned to HF; its position was identical to that of a solution of HF in sulfuric acid.

The observed NMR peaks are those which would be expected for the N-fluoro-N-methylisopropylidenimmonium ion, a species having carbonium and immonium resonance contributions.

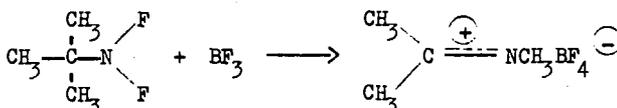


Thus, the F^{19} spectrum indicates coupling of a fluorine to three protons. The proton doublet at 4.09 p.p.m. is assigned to the N-methyl group and the 156 c.p.s. peak, to the C-methyls.

The formation of the N-fluoro-N-methylisopropylidenimmonium ion can be rationalized as a nucleophilic methyl migration with fluoride leaving:



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 white solid precipitated. This solid was filtered under nitrogen and was dried under vacuum to give a 60% yield of N-fluoro-N-methylisopropylidenimmonium fluoborate.



This salt was extremely hygroscopic, but a satisfactory elemental analysis was obtained on a sample that was handled in a dry box.

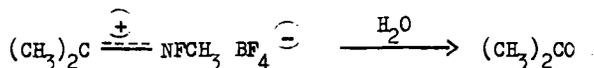
Anal. Calc'd for $C_4H_9NF_5B$: C, 27.1; H, 5.08; N, 7.91; F, 53.6.

Found: C, 26.9; H, 5.22; N, 7.80; F, 51.9.

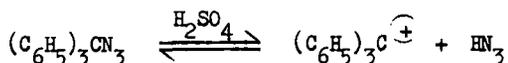
The reaction of *t*-butyldifluoramine with boron trifluoride also took place in the absence of solvent at -78° , and in liquid sulfur dioxide at its boiling point.

The proton NMR spectrum of the fluoborate was obtained using concentrated sulfuric acid as the solvent. The resulting spectrum was identical to that of the solution that was prepared by treating *t*-butyldifluoramine with concentrated sulfuric acid. The F^{19} NMR spectrum of this solution consisted of a quartet at -141.5 p.p.m., with a coupling constant of 18.5 c.p.s., and singlets at -116.9 p.p.m. and $+67.5$ p.p.m. 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 fluoboric acid to concentrated sulfuric acid. The -116.9 p.p.m. band corresponds to HF but the $+67.5$ p.p.m. band is shifted somewhat from that of a solution of BF_3 in sulfuric acid ($+65.82$ p.p.m.). The equilibrium of BF_4^- with HF and BF_3 is well known in aqueous solutions.⁴

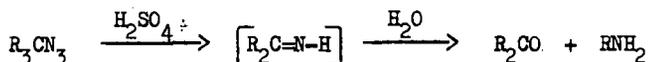
Although the fluoborate was very hygroscopic and decomposed rapidly when it was exposed to the atmosphere, it did not change under prolonged storage under dry nitrogen at room temperature. The addition of the salt to water gave acetone, which was isolated as its 2,4-dinitrophenylhydrazone.



The different paths followed by the reactions of trityldifluoramine and *t*-butyl-difluoramine with acids, C-N cleavage for the former and N-F cleavage with rearrangement for the latter, are paralleled by the reactions of the corresponding azides with sulfuric acid. Thus, trityl azide in concentrated sulfuric acid exists in equilibrium with the trityl cation and hydrazoic acid.⁵



Tertiary alkyl azides, on the other hand, rearrange to the corresponding Schiff bases.⁶



The N-fluoro-N-methylisopropylidenimmonium salts are the first members of a new class of compounds potentially useful in organic synthesis. The generality of the rearrangement of alkylidifluoramines catalyzed by Lewis or protonic acids is being investigated.

Acknowledgement

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