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BECKMANN FRAGMENTATION OF α-DIFLUORAMINO FLUORIMINES; A ROUTE TO α-DIFLUORAMINO FLUORIDES

Travis E. Stevens
Rohm and Haas Company
Redstone Research Laboratories
Huntsville, Alabama 35807

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Two recent communications have reported examples of oximes undergoing Beckmann fragmentation with substitution of chloride ion at the tetrahedral α-carbon atom.[1,2] Instead of a double bond being produced by proton loss from the presumed carbonium ion intermediate, chloride ion trapped the carbonium ion. In the first example, 1,1-diaryl-2-propanone oximes were converted to benzhydryl chlorides[1] by phosphorus pentachloride in ether; the second example was the isolation of 6-chloro-6-methoxyhexanenitrile from cleavage of 2-methoxycyclohexanone oxime with thionyl chloride.[2]

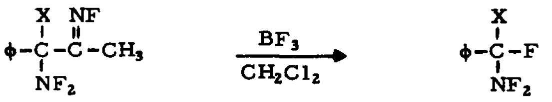
We wish to report that α-difluoramino fluorimines (Ia, b, c, IIIa, b) in the presence of boron trifluoride in methylene chloride produce α-difluoramino fluorides (IIa, b, c, IVa, b), apparently by way of fragmentation of the fluorimine and trapping of the intermediate α-difluoramino carbonium ion by fluoride ion. The yields ranged from 25% (IIc, IV) to 68% (IIa).

The fluorimines (I and III) were obtained by addition of tetrafluorohydrazine to the appropriate olefin,[3,4] followed by dehydrofluorination of the secondary difluoramino function with sodium methoxide in methanol. All samples had elemental analyses and NMR spectra (H^1 and F^{19}) consistent with the structural formulations.

An example of the Beckmann reaction, the conversion of Ia to IIa, follows: A mixture of 5 ml. of methylene chloride, 0.71 g (3 mmoles) of Ia and 70 cc (STP) of boron trifluoride were stirred in a sealed 25 ml. pressure tube[5] at -10° for 10 minutes and at 0° for one hour. The tube was vented, and the residue, diluted with methylene chloride, was washed with water and aqueous sodium bicarbonate solution. The organic layer was fractioned *in vacuo* through -45° and -80° traps. The -45° trap retained IIa, a clear liquid, 0.40 g.

Anal.

Calc'd. for $C_7H_5ClNF_3$: C, 42.99; H, 2.58; N, 7.16; F, 29.1; Cl, 18.1.
Found: C, 43.28; H, 2.87; N, 7.89; F, 29.6; Cl, 18.2.



Ia, X = Cl

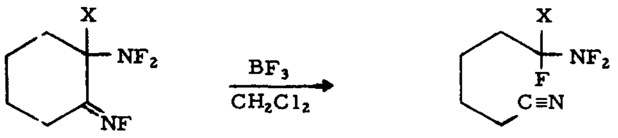
Ib, X = Br

Ic, X = CH_3

IIa, X = Cl

IIb, X = Br

IIc, X = CH_3



IIIa, X = Cl

IIIb, X = CH_3

IVa, X = Cl

IVb, X = CH_3

Since the two fluorines of the $-NF_2$ function are magnetically non-equivalent due to asymmetric carbon, the F^{19} NMR spectrum of IIa is of the ABX type.[6] The fluorines of the difluoramino group are not shifted appreciably from one another; F_A is about -31.8ϕ and F_B is about -31ϕ with strong coupling (J_{AB} = 588 cps). The C-F resonance is at + 104.3 and the coupling of both $-NF_2$ fluorine nuclei appear to be about 8 cps. This appears as a deceptively simple 1:2:1 triplet.[6] Decoupled from the $-NF_2$ fluorines, this resonance is a singlet.

Although fragmentation appeared to be the major reaction of the α-halo-α-difluoraminofluorimines Ia, Ib and IIIa, other processes leading to amides or amide-like materials accounted for the low yields of cleavage products of Ic and IIIb. These materials have resisted characterization, and in view of the possibility of further rearrangement of organic difluoramines in the presence of boron trifluoride,[7] they may be complex mixtures.[8]

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5. Described by R. P. Rhodes, J. Chem. Ed., 40, 423 (1963).
6. For a detailed discussion of the F^{19} NMR spectrum of 1,2-bis(difluoramino) 1,2-diphenyl ethane see F. A. Johnson, C. A. Haney and T. E. Stevens, J. Org. Chem., 32, 466 (1967); for a similar treatment of 1-difluoramino-1-fluoro-2-fluorimino-1,2-diphenylethane see R. C. Petry, et. al., J. Org. Chem., 32, 0000 (1967).
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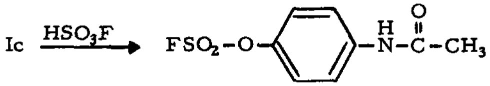
8. For example, the reaction of Ic and fluorosulfonic acid in methylene chloride produced 4-fluorosulfatoacetanilide (i). This fluorosulfation probably involved a N-phenyl-N-



i

fluoroammonium salt; at least such an intermediate allows one to draw an analogy with the Wallach rearrangement. And indeed, azoxybenzene gives 4-fluorosulfatoazobenzene when treated with HSO_3F. (Unpublished observations.)