

Rearrangements of Organic Difluoramines. Aromatic Nucleophilic Rearrangements in Fluorosulphonic Acid

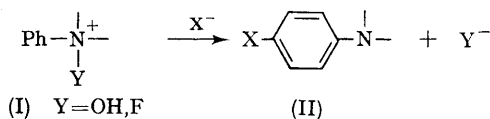
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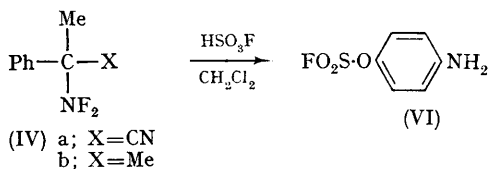
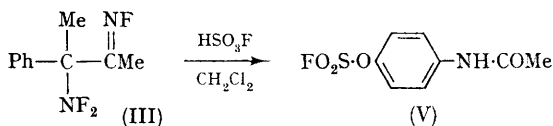
SEVERAL examples of aromatic rearrangements and substitutions, which result in a nucleophile becoming attached to an aromatic ring, seem to fit the category called "aromatic nucleophilic rearrangements".¹ These include the aromatic hydroxylamine-aminophenol case cited,¹ the

Wallach rearrangement,² the acid-promoted cleavage of aromatic nitrones to *para*-substituted phenols,³ the rearrangement of *NN*-dimethylaniline oxide,⁴ and the rearrangements of the α -difluoramino toluene derivatives reported here. All these examples, at least formally, appear to

have as an intermediate, an aromatic ring attached to a quadrivalent, positively-charged nitrogen bearing a leaving group. [see (I)].⁵



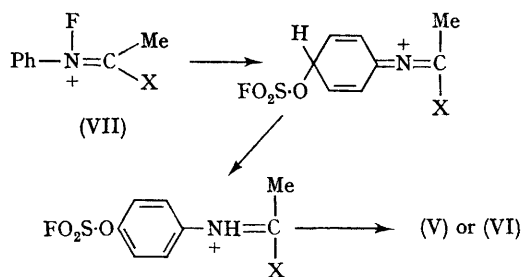
Of most interest here are the products from the three α -(difluoramino)toluenes (III) and (IVa, b); fluorosulphates (V) and (VI) are produced in reactions conducted in methylene chloride solution at ambient temperature.[†]



In view of the tendency of organic difluoramino-compounds to rearrange with loss of fluoride from nitrogen,⁶ it appears that the first step in the process leading to fluorosulphate is migration of

the aryl group to nitrogen to produce an *N*-aryl-*N*-fluoroimmonium salt such as (VII). The fluoroborate of (VII; X = Me), has been prepared from (IVb) and BF₃ in pentane solution, and characterized by n.m.r. spectra.[‡] Indeed, (VI) is formed when this salt is exposed to fluorosulphonic acid.

Further reaction of salts such as (VII) in the manner outlined, and apparently related to the rearrangements discussed above, produces (V) or (VI). With (III), X may be -OSO₂F, since Beckmann fragmentation of the fluorimine probably occurs first,⁷ and related fluorosulphates have been isolated.



N-Phenylhydroxylamine and fluorosulphonic acid in methylene chloride solution at ice-bath temperature produced (VI) cleanly. The nitrene, *N*-phenylbenzaldoxime, was also converted into (VI), but neat fluorosulphonic acid at steam-bath temperature was required. However, *N*-(*p*-tolyl)-hydroxylamine was reduced to *p*-toluidine by fluorosulphonic acid.

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[†] All compounds reported here gave acceptable elemental analyses and had infrared and n.m.r. spectra compatible with the assigned structure.

[‡] The ¹⁹F n.m.r. spectrum exhibited peaks at -90.7 ϕ (NF) and +150.4 ϕ (BF₄⁻); the proton spectrum had non-equivalent methyl groups at 2.92 and 2.61 δ , each a doublet, $J_{\text{HF}} = 5$ and 3 c./sec., respectively.

¹ C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N.Y., pp. 621-624.

² E. C. Buncl and B. T. Lawton, *Canad. J. Chem.*, 1965, **43**, 862; L. C. Behr and E. C. Hendley, *J. Org. Chem.*, 1966, **31**, 2715; M. M. Shemyakin, V. I. Maimind, and T. E. Agadzhanian, *Chem. and Ind.*, 1961, 1223; C. S. Hahn and H. H. Jaffe, *J. Amer. Chem. Soc.*, 1962, **84**, 946; S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc. Japan*, 1963, **36**, 601; For a recent review, see P. A. S. Smith "Open-Chain Nitrogen Compounds" Vol. 2, W. A. Benjamin, Inc., New York, 1966, pp. 313-315.

³ E. Bamberger, *Ber.*, 1894, **27**, 1556.

⁴ E. Bamberger and P. Seyden, *Ber.*, 1901, **34**, 12; A. F. Douglas, P. H. Gore, and J. W. Hooper, *J. Chem. Soc.*, (C), 1967, 674, report related reactions.

⁵ The formal comparisons should be emphasized here; the timing and details of the processes involved may be very different. And, in the Wallach rearrangement, nucleophilic attack may occur in the ring attached to oxidized nitrogen or in the far ring (as often postulated). For pertinent comments see P. H. Gore, *Chem. and Ind.*, 1959, 191.

⁶ K. Baum and H. M. Nelson, *J. Amer. Chem. Soc.*, 1966, **88**, 4457.

⁷ T. E. Stevens, *Tetrahedron Letters*, 1967, 3017.