Rearrangements of Organic Fluoramines. Aromatic Nucleophilic Rearrangements in Fluorosulfonic Acid

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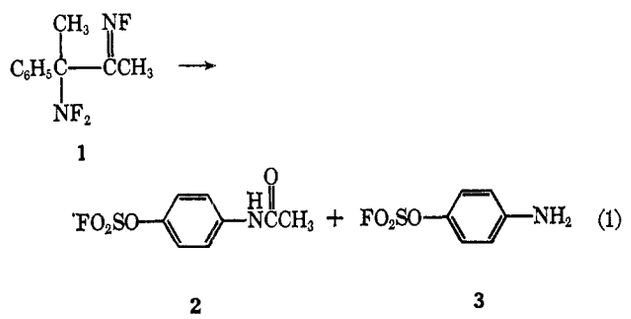
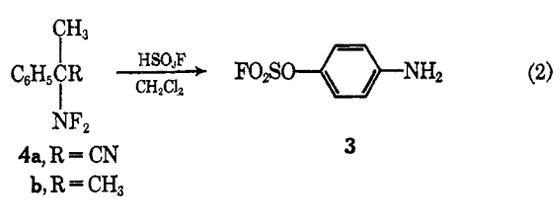
The rearrangement of the α-(difluoramino)toluene derivatives **1**, **4a**, and **4b** in fluorosulfonic acid produces 4-(fluorosulfato)anilines. This rearrangement probably proceeds by way of an N-phenyl-N-fluorimmonium salt, and is similar to the acid-promoted rearrangements of other oxidized nitrogen compounds, such as aromatic hydroxylamines, nitrones, azoxybenzenes, and aniline N-oxides.

During a study of acid-catalyzed reactions of α-difluoramino fluorimines, certain reactions conducted in fluorosulfonic acid led to products reminiscent of rearrangements of oxidized nitrogen compounds. Specifically, it was observed that fluorimine **1**, under conditions intended to lead to Beckmann rearrangement or fragmentation,[1] was converted into 4-(fluorosulfato)acetanilide (**2**), mp 146–148° (up to 44% yield),[2] along with lesser amounts of 4-(fluorosulfato)aniline (**3**), 4-aminophenol, and acetophenone (eq 1). α-(Difluoramino)toluenes **4a** and **b** were con-



1 **2** **3** (1)

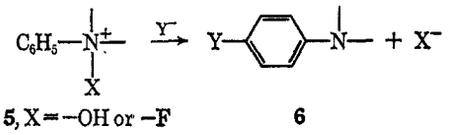
verted into 4-(fluorosulfato)aniline (**3**) under the same reaction conditions (eq 2). This paper reports a



4a, R = CN
b, R = CH_3 **3** (2)

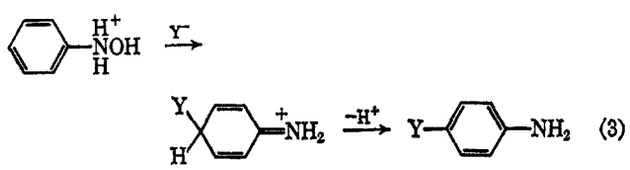
study of these reactions and of other apparently analogous rearrangements.

The incorporation of a nucleophile into the *para* position of an aromatic ring attached to an oxidized nitrogen atom is, of course, characteristic of aromatic rearrangements and substitutions called "aromatic nucleophilic rearrangements."[3] It does not appear to be generally recognized, however, that nucleophilic substitution may take place whenever an aromatic ring is attached to a tetravalent, positively charged nitrogen atom bearing a leaving group (**5** → **6**). Thus, the examples that at least formally[4] appear to fall in this category include the aromatic hydroxylamine–aminophenol case cited,[2] the Wallach rearrangement,[5–8] the acid-promoted cleavage of aromatic nitrones to *para*-substituted phenols,[9] the rearrangement of N,N-dimethylaniline oxide to *p*-dimethylaminophenol,[10] and the organodifluoramine rearrangements reported here.



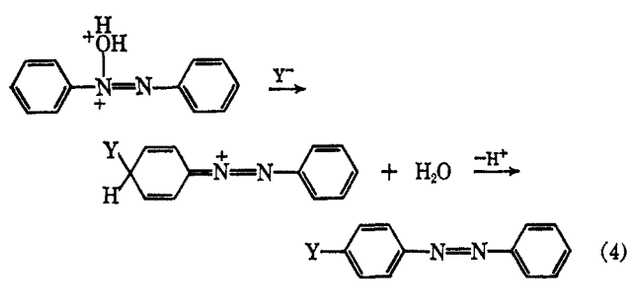
5, X = −OH or −F **6**

In the context of structure **5**, the hydroxylamine rearrangement can be formulated as shown[3] in eq 3 and



(3)

the Wallach rearrangement[4,7] as shown in eq 4. The



(4)

possibility of S_N2' mechanism for the hydroxylamine reaction[2] and the kinetic evidence for the intermediacy of a dicarbonium ion in the Wallach rearrangement[4,6] must be noted.

Now, if the first step in the conversion of difluoramine **1** into fluorosulfate **2** (Scheme I) is the migration of the phenyl group to nitrogen to produce N-phenyl-N-fluorimmonium salt **7**,[11] this reaction falls into the aromatic

(1) T. E. Stevens, *Tetrahedron Lett.*, 3017 (1967).

(2) A preliminary account of this work has appeared: T. E. Stevens, *Chem. Commun.*, 1181 (1967).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1950, pp 621–624.

(4) 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. Ind.* (London), 191 (1959).

(5) (a) E. C. Buncel and B. T. Lawton, *Can. J. Chem.*, **43**, 862 (1965); (b) M. M. Shemyakin, V. I. Maimind, and T. E. Agadzhanyan, *Chem. Ind.* (London), 1223 (1961).

(6) C. S. Hahn and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 946 (1962); C. S. Hahn, K. W. Lee, and H. H. Jaffé, *ibid.*, **89**, 4975 (1967).

(7) S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc., Jap.*, **36**, 601 (1963).

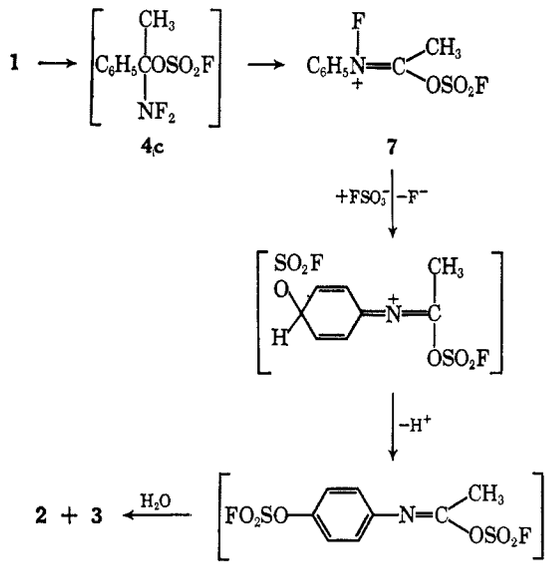
(8) For a recent review, see P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, pp 313–315.

(9) E. Bamberger, *Ber.*, **27**, 1556 (1894).

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

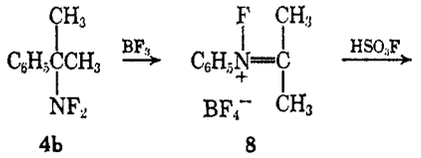
(11) Beckmann fragmentation of the fluorimine probably occurs first,[1] and fluorosulfonic acid may then trap the α-difluoramino carbonium ion to give **4c**. In certain cases, such fluorosulfates have been isolated (unpublished studies). The formation of structures such as **4c** and **7** explains the formation of the acetanilide **2** along with free amine **3**. Also, acetophenone, from hydrolysis of **4c** or the carbonium ion, was the major by-product here.

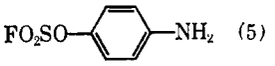
SCHEME I



nucleophilic substitution class also. In view of the tendency of organic compounds to rearrange with loss of fluoride ion from nitrogen,[12] such a process appears likely.

Strong support for the reaction scheme outlined was obtained from experiments with the organic difluoramine **4b**. This difluoramine, prepared by the acid-catalyzed addition of difluoramine to α-methylstyrene,[13] was converted into N-phenyl-N-fluoroisopropylidenimmonium fluoroborate (**8**) by boron trifluoride in pentane or methylene chloride solution (eq 5). The salt **8** was characterized only by its nmr spec-





(5)

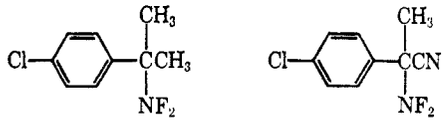
tra; its ^{19}F spectrum exhibited peaks at ϕ −90.7 (NF) and at +150.4 (BF_4^-), and the proton spectrum had nonequivalent methyl groups at δ 2.92 and 2.61 (doublets, J_{HF} = 5 and 3 Hz, respectively). When fluorosulfonic acid was added to **8** in methylene chloride solution, aniline **3** (68%) could be isolated after hydrolysis.

Aniline **3** (21% yield) also was prepared directly from α-methylstyrene, difluoramine, and fluorosulfonic acid. Under these conditions, ionic addition of difluoramine to the olefin should be followed by rearrangement and then nucleophilic substitution.

It was not possible to prepare an N-fluorimmonium salt from **4a** and boron trifluoride; the nitrile function apparently complexed the BF_3. However, with an excess of boron trifluoride and an extended reaction time, 4-fluoroaniline (22%) formed from **4a**. And, fluorosulfonic acid converted **4a** into **3** (45% yield) readily.

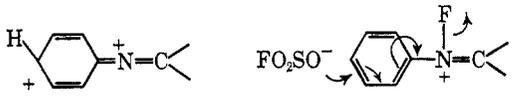
(12) K. Baum and H. M. Nelson, *J. Amer. Chem. Soc.*, **88**, 4457 (1966).
(13) W. H. Graham and J. P. Freeman, *ibid.*, **89**, 716 (1967).

No definitive products could be obtained from related difluoramines (**9** and **10**) in which the 4 position was

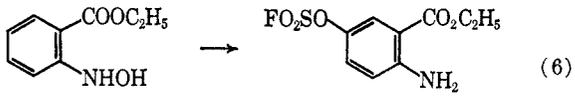


blocked. Although **9** rearranged readily in the presence of boron trifluoride to give N-(4-chlorophenyl)-N-fluoroisopropylidenimmonium fluoroborate,[14] only intractable products resulted from treatment of this salt with fluorosulfonic acid. Excess boron trifluoride and **10** also gave dark, intractable materials.

Although there appears to be little doubt that the rearrangements reported here proceed by mechanisms analogous to those discussed above, a detailed description of the process leading from N-fluorimmonium salt to the 4-fluorosulfato aniline cannot be made on the basis of the information at hand. Suffice it to say that it probably involves intermediates between the extremes of dication **11** and an SN2′ process sketched as **12**.



It was also of interest to observe the rearrangements of some of the oxidized nitrogen compounds in the presence of fluorosulfonic acid.[15] Aromatic hydroxylamines with the *para* position open were readily converted into 4-(fluorosulfato)anilines by fluorosulfonic acid at ice-bath temperatures. Aniline **3** was obtained in 54% yield from N-phenylhydroxylamine; acetylation of **3** produced in this way gave samples of **2** identical with those isolated from fluorimine **1**; and N-(3-chlorophenyl)hydroxylamine gave 3-chloro-4-(fluorosulfato)aniline in 56% yield.[16] Hydroxylamine **13** gave the ester **14** (53%).[16]



(6)

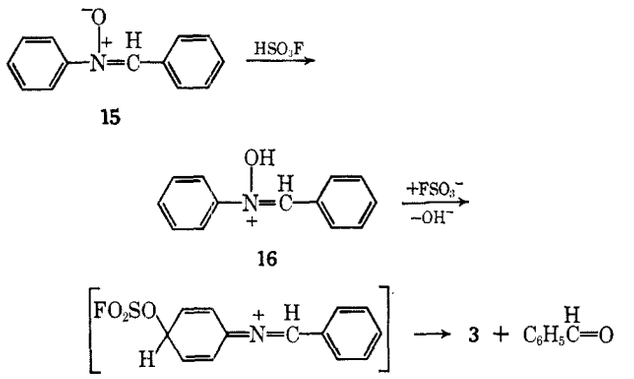
p-Tolylhydroxylamine was reduced to *p*-toluidine (42%) by fluorosulfonic acid. The fate of the oxygen atom, or the nature of the oxidizing species resulting from the reduction, is unknown. No oxygen was produced in the experiments, no active oxygen material could be detected in the reaction mixtures, and azobenzene introduced into the reaction mixture was not oxidized.[15] Of course, either starting material or *p*-toluidine could have been oxidized during the course of the reaction.

As expected,[9] the nitrone N-phenylbenzaldoxime (**15**) gave benzaldehyde (52%) and aniline **3** (38%) when exposed to fluorosulfonic acid; however, steam-bath

(14) Characterized by ^{19}F nmr spectrum peaks at ϕ −91.5 (NF) and +150.9 (BF_4^-), and proton nmr spectrum methyl peaks at δ 2.88 (doublet, J_{HF} = 5 Hz) and 2.67 (doublet, J_{HF} = 3 Hz).
(15) The Wallach rearrangement in fluorosulfonic acid and in fluorosulfonic acid–difluoramine is discussed in another paper: T. E. Stevens, *J. Org. Chem.*, **33**, 2667 (1968).
(16) In these experiments no attempt was made to isolate any phenolic amine produced by hydrolysis of the fluorosulfate.

temperatures were required for this transformation. The probable course of this reaction is outlined in Scheme II. Again, either a dication from ionization of **16** or an SN2′ process involving **16** can be visualized.

SCHEME II



Certain spectral properties of the aromatic fluorosulfates prepared here allow them to be recognized easily. The ^{19}F nmr spectra of the fluorosulfates exhibit a peak in the ϕ −40 to −35 region, somewhat higher field than aliphatic perfluorofluorosulfates.[17] Specific values for the fluorosulfates prepared here are reported in the Experimental Section. The most characteristic peak in the infrared spectra of the fluorosulfates was the symmetric S=O stretch at 8.1 μ.[17] The asymmetric S=O stretching band at 6.70–6.75 μ[17] was also observed. Strong infrared absorption (unassigned) was also noted in the 10.8–11.2-μ region.

Finally, attempts to prepare aromatic difluoramines[18] by using difluoramine as the nucleophile in these rearrangements were completely unsuccessful. There was no sign of aromatic NF materials when salt **8** was exposed to difluoramine in the presence of BF_3 or HSO_3F; the same was true when N-phenylhydroxylamine, HNF_2, and HSO_3F were allowed to interact. Some 4-(fluorosulfato)aniline, or 4-fluoroaniline when BF_3 was used, could be obtained along with intractable material. It is possible that the 4-(difluoramino)anilines, if they form at all, are unstable to the reaction conditions.[18]

Experimental Section

The ^{19}F nmr spectra (40 MHz) were run in CCl_4 or $CDCl_3$ solutions; ϕ values are measured in parts per million (ppm) from internal CCl_3F. Melting points are uncorrected. Proton nmr spectra were run on a Varian A-60 spectrometer. Fluorosulfonic acid was Baker and Adamson technical grade. Methylene chloride was dried by passage through a silica gel column. Chromatogaphy on Brinkmann or G. F. Smith silica gel was conducted by packing the column in pentane; elution with pentane containing increasing amounts of methylene chloride followed. Finally, methylene chloride–ethyl acetate (9:1) and methylene chloride–methanol (9:1) completed the elution.

Previous warnings[13,19] concerning the explosive nature of difluoramine and of organic difluoramino compounds must be heeded.

2-Difluoramino-2-phenyl-3-fluoriminobutane (**1**), a colorless liquid, was prepared by dehydrofluorination of the α,β-dimethylstyrene–tetrafluorohydrazine adduct with sodium methoxide in methanol,[19] bp 64° (0.3 mm). Purification was best effected by passage through a silica gel column. Elution with pentane–methylene chloride (10:1) gave pure **1**: ^{19}F nmr, $-NF_2$, AB quartet; F_A, ϕ −30.0; F_B, −25.0 (J_{FF}, 582 Hz); C=NF, single peak at −28.6.

Anal. Calcd for $C_{10}H_{11}F_3N_2$: C, 55.55; H, 5.13; N, 12.96. Found: C, 55.35; H, 5.27; N, 13.45.

2-Difluoramino-2-phenylpropane (**4b**) was prepared by the addition of difluoramine to α-methylstyrene.[13] From 0.47 g of α-methylstyrene, 110 cc (STP) of difluoramine, 2 ml of methylene chloride, and 0.1 g of Amberlyst 15, stirred 4 hr at ambient temperature and pressure, was obtained 0.36 g of **4b**, isolated by distillation *in vacuo* into a −10° trap. The ^{19}F nmr spectrum exhibited a single peak at ϕ −29.2.

Anal. Calcd for $C_9H_{11}F_2N$: C, 63.1; H, 6.48; N, 8.18. Found: C, 62.7; H, 6.61; N, 7.94.

2-Difluoramino-2-(4-chlorophenyl)propane (**9**) was prepared in the same way; 0.62 g of 4-chloro-α-methylstyrene gave 0.48 g of **9**.

Anal. Calcd for $C_9H_{10}ClF_2N$: C, 52.6; H, 4.90; N, 6.81; F, 18.5. Found: C, 53.0; H, 5.39; N, 6.59; F, 18.7.

Fluoramines **4a** and **10** were prepared as reported.[19]

Reaction of Fluorosulfonic Acid and 2-Difluoramino-2-phenyl-3-fluoriminobutane (**1**).—To a mixture of 4 ml of methylene chloride and 4 ml of fluorosulfonic acid cooled to 0° was added 0.86 g (4 mmol) of **1** in 2 ml of methylene chloride. The mixture was stirred at 0° for 1 hr and at ambient temperature for 3 hr. The mixture was poured into ice water and the organic product was extracted into methylene chloride. The residue obtained upon evaporation of the methylene chloride was pumped *in vacuo;* a −10° trap collected 0.05 g (10%) of acetophenone, identified by infrared and nmr spectra. The solid residue, mp 132–137°, 0.24 g (27%), was crude 4-(fluorosulfato)acetanilide. After further recrystallization from chloroform–hexane, **2** had mp 146–148°. The ^{19}F nmr of **2** had a peak at ϕ −36.9; the proton nmr had peaks at τ 7.83 (CH_3–CO) and 2.2–2.8 (aromatic protons).

Anal. Calcd for $C_8H_8NFO_4S$: C, 41.20; H, 3.46; N, 6.01. Found: C, 41.35; H, 3.84; N, 6.06.

To 0.15 g of **2** in 10 ml of 90% methanol was added 2 ml of 1.3 *N* sodium methoxide in methanol. The mixture was refluxed for 30 min, cooled, acidified, and stripped to dryness. To the residue was added 10 ml of acetic anhydride and 1 drop of concentrated sulfuric acid. After stirring overnight, the mixture was poured into water and stirred 2 hr. The organic product, isolated by extraction into methylene chloride, melted at 147–148° after recrystallization from chloroform–pentane; 4-acetoxyacetanilide has reported mp 152°.[20] The 4-acetoxyacetanilide prepared from **2** was identical, by infrared and proton nmr spectra and mixture melting point (146–147°), with a sample prepared (mp 146–147°) by acetylation of 4-hydroxyacetanilide (Eastman).

The acid aqueous phase was basified and again extracted with methylene chloride. Evaporation of the methylene chloride gave 0.19 g (25%) of 4-(fluorosulfato)aniline (**3**), mp 41–42.5° (chloroform–hexane). The ^{19}F nmr spectrum had a peak at ϕ −35.5.

Anal. Calcd for $C_6H_6FNO_3S$: C, 37.7; H, 3.16; N, 7.33; F, 9.94. Found: C, 37.5; H, 3.04; N, 7.24; F, 10.2.

The aqueous layer was made acidic stripped to dryness, and treated with acetic anhydride (10 ml) as described above. After work-up of the reaction mixture, 0.16 g (21%) of 4-acetoxyacetanilide was obtained from the soluble 4-aminophenol.

Up to 44% of **2** was obtained in other runs, along with lesser quantities of **3**.

Reaction of 2-Difluoramino-2-phenylpropanenitrile (**4a**) **and Fluorosulfonic Acid.**—To 5 ml of fluorosulfonic acid cooled in an ice bath was added 0.90 g (5 mmol) of **4a** in 5 ml of methylene chloride. The mixtue was stirred at 30° for 4 hr, then poured on ice–dilute aqueous hydrochloric acid. Extraction with methylene chloride gave less than 0.2 g of material; this was discarded. The aqueous layer was made basic and again extracted with methylene chloride. This yielded 0.43 g of 4-(fluorosulfato)-aniline (**3**), mp 41–42.5°.

Reaction of N-Phenyl-N-fluoroisopropylidenimmonium Fluoroborate (**8**) **and Fluorosulfonic Acid.**—A mixture of 0.17 g (1 mmol) of 2-difluoramino-2-phenylpropane (**4b**), 25 cc (STP) of boron trifluoride, and 5 ml of methylene chloride in the pressure tube[21]

(17) M. Lustig and J. K. Ruff, *Inorg. Chem.*, **3**, 287 (1964); M. Lustig, *ibid.*, **4**, 1828 (1965).

(18) C. L. Coon, M. E. Hill, and D. L. Ross, Abstracts, 154th National Meeting of the American Chemistry Society, Chicago, Ill., Sept 1967, p S123.

(19) R. C. Petry and J. P. Freeman, *J. Org. Chem.*, **32**, 4034 (1967).

(20) L. Galatis, *Ber.*, **59**, 846 (1926).

(21) Described by R. P. Rhodes, *J. Chem. Educ.*, **40**, 423 (1963).

was stirred at ice-bath temperature for 1 hr, warmed briefly to 20°, and cooled to 0°, and excess boron trifluoride was vented (the ^{19}F and proton nmr spectra of **8** prepared in this way, or in pentane solution, had the properties described in the discussion section). To the stirred mixture at 0° was added 0.5 ml of fluorosulfonic acid. The contents of the tube were stirred for 1 hr at 0°, and then poured over ice–dilute aqueous hydrochloric acid. A methylene chloride extract was discarded; the aqueous layer was basified and again extracted. From this methylene chloride extract was obtained 0.13 g (68%) of **3**, mp 40–41°.

Reaction of α-Methylstyrene, Difluoramine, and Fluorosulfonic Acid.—A mixture of α-methylstyrene (0.39 ml, 3 mmol), 70 cc (STP) of difluoramine, 1 ml of fluorosulfonic acid, and 5 ml of methylene chloride was stirred 90 min at 0° in a 25-ml pressure tube.[21] The tube was vented *in vacuo*, and the residue was worked up as usual. Extraction of the basified aqueous layer gave **3**: yield, 0.12 g (21%); mp 38.5–40.5°.

Reaction of 2-Difluoramino-2-phenylpropanenitrile (4a) and Boron Trifluoride.—A mixture of 0.55 g of **4a** (3 mmol), 70 cc (STP) of boron trifluoride, and 5 ml of methylene chloride was stirred 5 hr at ambient temperature in a pressure tube. The tube was the vented and the reaction mixture poured on ice–hydrochloric acid. The extract from the basified aqueous layer was chromatographed on silica gel and gave 4-fluoroaniline 0.074 g (22%), identified by comparison of its infrared spectrum, and its ^{19}F and proton nmr spectra with those of a authentic sample. The ^{19}F nmr peak of 4-fluoroaniline was observed at ϕ +126.1.

Reaction of N-Phenylhydroxylamine and Fluorosulfonic Acid.—To 3 ml of fluorosulfonic acid stirred at ice bath temperature was added 1 g of N-phenylhydroxylamine in 4 ml of methylene chloride. After 2 hr at ice bath temperature, the mixture was poured on ice. Only a trace of material could be extracted from the acidic aqueous layer; on the basic side, 0.95 g (54%) of **3** was extracted. A 0.65-g portion of **3** prepared in this way was acetylated with 10 ml of acetic anhydride and 1 drop of concentrated sulfuric acid. After hydrolysis of excess acetic anhydride, 0.60 g of **2**, mp 145–147°, infrared and nmr spectra identical with that of **2** prepared from **1**, was obtained.

The aqueous phase from the fluorosulfonic acid reaction was acidified, stripped to dryness, and acetylated with acetic anhydride. In this way, 0.13 g of 4-acetoxyacetanilide (7%) was obtained.

Reaction of N-(3-Chlorophenyl)hydroxylamine and Fluorosulfonic Acid.—The procedure used with N-phenylhydroxylamine was followed. From 2 g of the hydroxylamine was obtained 1.76 g of 3-chloro-4-(fluorosulfato)aniline, a clear liquid that darkened on standing. The ^{19}F nmr spectrum peak was at ϕ −39.3. A sample chromatographed on silica gel gave the following analysis.

Anal. Calcd for $C_6H_5ClFNO_3S$: C, 31.94; H, 2.23; N, 6.21. Found: C, 32.59; H, 2.20; N, 6.22.

The *p*-toluenesulfonyl derivative of 3-chloro-4-(fluorosulfato)-aniline had mp 121–123°. The ^{19}F nmr spectrum had a peak at ϕ −41.1.

Anal. Calcd for $C_{13}H_{11}ClFNO_5S_2$: C, 41.1; H, 2.92; N, 3.69. Found: C, 41.5; H, 3.34; N, 3.64.

Reaction of Fluorosulfonic Acid and Ethyl 2-(Hydroxylamino)-benzoate (13).—The reaction was carried out at ice-bath temperature using 1.71 g (10 mmol) of **13**, 3 ml of fluorosulfonic acid, and 5 ml of methylene chloride. After the usual hydrolysis, a total of 1.4 g of ethyl 2-amino-4-(fluorosulfato)benzoate (**14**), a liquid, was recovered from both the acidic aqueous phase (1.1 g) and the basic aqueous phase (0.3 g). A satisfactory elemental analysis on **14** could not be obtained. The ^{19}F nmr spectrum had a peak at ϕ −35.6. The *p*-toluenesulfonyl derivative of **14** melted at 105–107°.

Anal. Calcd for $C_{16}H_{16}FNO_7S_2$: C, 46.04; H, 3.86; N, 3.35. Found: C, 46.05; H, 3.91; N, 3.43.

Reaction of N-Phenylbenzaldoxime (15) and Fluorosulfonic Acid.—A mixture of 0.78 g (3.96 mmol) of **15** and 3 ml of fluorosulfonic acid was heated on the steam bath for 30 min. The mixture was cooled, hydrolyzed, and extracted as usual. From the aqueous acid layer came 0.37 g of a mixture of benzaldehyde (0.22 g, 52%) and **3**, 0.15 g (by infrared and proton nmr spectra). The basic layer gave an additional 0.14 g of **3**, mp 39–40°.

Registry No.—Fluorosulfonic acid, 7789-21-1; **1**, 16704-36-2; **2**, 16704-37-3; **3**, 16704-38-4; **4b**, 16704-39-5; **9**, 16704-40-8; 3-chloro-4-(fluorosulfato)aniline, 16704-41-9; *p*-toluenesulfonyl derivative of 3-chloro-4-(fluorosulfato)aniline, 16704-42-0; *p*-toluenesulfonyl derivative of **14**, 16704-43-1.

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Reaction of Azoxy Compounds with Fluorosulfonic Acid and Fluorosulfonic Acid–Difluoramine[1]

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Azoxybenzenes unsubstituted in the 4 or 4′ position are converted into 4-fluorosulfatoazobenzenes by the Wallach transformation in fluorosulfonic acid. With added difluoramine, azoxybenzenes with both 4 positions open produce 4,4′-diaminoazobenzenes. Evidence for intermolecular transfer of oxygen between azoxybenzenes is reported. Some rearrangements apparently related to the Wallach rearrangement are discussed.

Our interest in the Wallach rearrangement, the conversion of azoxybenzene and its derivatives into 4-substituted azobenzenes, in the presence of fluorosulfonic acid was prompted by our interest in related aromatic nucleophilic substitutions in this medium,[2] and by the possibility that difluoramine (HNF_2), a reagent known to be alkylated by carbonium ions in acid solutions,[3] might be incorporated into the Wallach product and lead to a difluoraminoazobenzene. It should be noted that attempts to utilize difluoramine in the same manner in the apparently related rearrangements of N-phenyl-N-fluoroimmonium salts and of N-phenylhydroxylamine failed.[2]

Among the studies of the Wallach rearrangement[4] in strong acids is the report that azoxybenzene and azoxybenzenes with an open 4 or 4′ position are converted into 4-chlorosulfatoazobenzenes by chlorosulfonic acid.[5] Kinetic studies which support a dication inter-

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(2) T. E. Stevens, *J. Org. Chem.*, **33**, 2664 (1968); T. E. Stevens, *Chem. Commun.*, 1181 (1967).

(3) W. H. Graham and J. P. Freeman, *J. Amer. Chem. Soc.*, **89**, 716 (1967).

(4) For a recent review, see P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, pp 313–315.

(5) V. O. Lukashevich and T. N. Sokolova, *Compt. Rend. Acad. Sci. URSS*, **54**, 693 (1946); *Chem. Abstr.*, **41**, 5472 (1947).