

was stirred at ice-bath temperature for 1 hr, warmed briefly to 20°, and cooled to 0°, and excess boron trifluoride was vented (the  $^{19}\text{F}$  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  $\alpha$ -Methylstyrene, Difluoramine, and Fluorosulfonic Acid.**—A mixture of  $\alpha$ -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.<sup>21</sup> 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 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  $^{19}\text{F}$  and proton nmr spectra with those of an authentic sample. The  $^{19}\text{F}$  nmr peak of 4-fluoroaniline was observed at  $\phi +126.1$ .

**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-phenylhydroxyl-

amine 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  $^{19}\text{F}$  nmr spectrum peak was at  $\phi -39.3$ . A sample chromatographed on silica gel gave the following analysis.

*Anal.* Calcd for  $\text{C}_6\text{H}_5\text{ClFNO}_2\text{S}$ : 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  $^{19}\text{F}$  nmr spectrum had a peak at  $\phi -41.1$ .

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{11}\text{ClFNO}_2\text{S}_2$ : 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  $^{19}\text{F}$  nmr spectrum had a peak at  $\phi -35.6$ . The *p*-toluenesulfonyl derivative of **14** melted at 105–107°.

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{16}\text{FNO}_2\text{S}_2$ : C, 46.04; H, 3.86; N, 3.35. Found: C, 46.05; H, 3.91; N, 3.43.

**Reaction of N-Phenylbenzaloxime (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<sup>1</sup>

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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,<sup>2</sup> and by the possibility that difluoramine ( $\text{HNF}_2$ ), a reagent known to be alkylated by carbonium ions in acid solutions,<sup>3</sup> 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.<sup>2</sup>

Among the studies of the Wallach rearrangement<sup>4</sup> 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.<sup>5</sup> Kinetic studies which support a dication inter-

(1) This research was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DA-01-021 AMC-11536(Z).

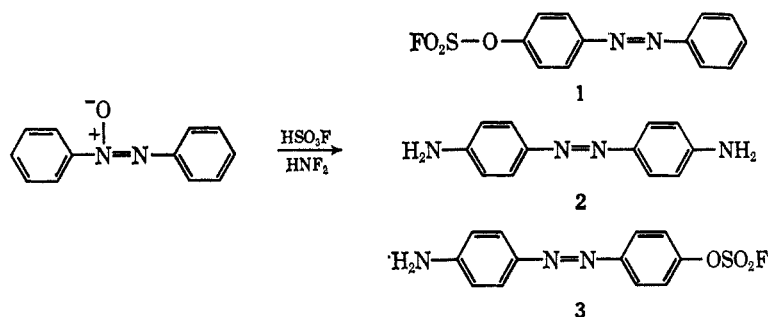
(2) T. E. Stevens, *J. Org. Chem.*, **33**, 2664 (1968); T. E. Stevens, *Chem. Commun.*, 1181 (1967).

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

SCHEME I

TABLE I  
4-FLUOROSULFATOAZOBENZENES

X	X'	Mp, °C	Yield, %	Anal., %						
				Calcd			Found			
H	H	98-100	71	C	H	N	C	H	N	<sup>19</sup> F nmr, $\phi^a$
H	4-Cl <sup>b</sup>	99-101	80	51.42	3.24	10.00	51.21	3.32	9.99	-37.4
H	4-Br <sup>c</sup>	88-90	61	45.79	2.56	8.90	45.50	2.60	8.80	-37.4
H	4-Cl <sup>d</sup>	77-79	48	40.12	2.24	7.80	40.12	1.80	7.48	-37.5
Cl	3-Cl <sup>d</sup>	77-79	48	41.28	2.02	8.20	41.48	2.35	8.22	-41.0
H	4-CH <sub>3</sub> <sup>e</sup>	79-81	10	53.05	3.77	9.52	53.40	3.82	9.70	-37.5

<sup>a</sup>  $\phi$  values in parts per million (ppm) from internal CCl<sub>3</sub>F in dilute CDCl<sub>3</sub> solution. <sup>b</sup> Registry no.: 16704-28-2; <sup>c</sup> 16704-29-3; <sup>d</sup> 16704-30-6; <sup>e</sup> 16704-31-7.

mediate<sup>6</sup> and labeling investigations<sup>7</sup> have also been published recently.<sup>8</sup>

It was, therefore, not surprising to find that azoxybenzene was converted cleanly into 4-(fluorosulfato)azobenzene by fluorosulfonic acid in methylene chloride under mild (0–25°) reaction conditions. Both 4- and 4'-chloroazoxybenzene gave the same product, 4-chloro-4'-(fluorosulfato)azobenzene, upon exposure to fluorosulfonic acid. The fluorosulfates prepared are listed in Table I; only with azoxybenzene was an attempt made to optimize the yield of fluorosulfate.

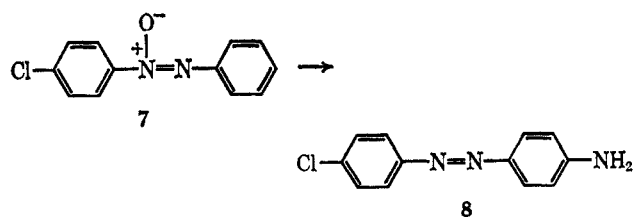
Three minor products accompanied the 4-(fluorosulfato)azobenzene produced from azoxybenzene; these were azobenzene (3%), a material (3%), mp 102–104°, that appeared to be 4-fluorosulfato-4'-hydroxyazobenzene, and a small amount of 4-hydroxyazobenzene. Formation of these materials will be discussed later. Both 4- and 4'-methylazoxybenzenes and fluorosulfonic acid gave considerable intractable material and only a low yield of fluorosulfate (Table I). On the basis of the normal position of the <sup>19</sup>F nmr peak and the indication of the only *para* substitution in the infrared spectrum, this product is assigned the 4-fluorosulfato-4'-methylazobenzene structure despite claims<sup>8b</sup> (disputed, however<sup>8b</sup>) that sulfuric acid and the 4-methylazoxybenzenes give 2'-hydroxy-4-methylazobenzene.

It was somewhat surprising to find that the products of the reaction of azoxybenzene, fluorosulfonic acid, and difluoramine (Scheme I) included, in addition to the usual Wallach fluorosulfate 1, two 4,4'-disubstituted

azobenzenes. These were 4,4'-diaminoazobenzene (2) and 4-amino-4'-(fluorosulfato)azobenzene (3). Under the experimental conditions outlined in the Experimental Section, yields of 1 ranged from 17 to 37%, yields of 2 ranged from 16 to 45%, and 3 was formed in yields of 5–20%. Excess difluoramine was present in these reactions, and a considerable portion of it was oxidized to tetrafluorohydrazine (N<sub>2</sub>F<sub>4</sub>) during the reaction. Thus, it appears likely that reduction of a fluoramino intermediate leads to the aminoazobenzenes.

With 3,3'-dichloroazoxybenzene, very analogous results were obtained (Scheme II). Fluorosulfate 4 (27–48.5%), the diaminoazo compound 5 (22–40%), and aminoazo fluorosulfate 6 (13–19%) could be isolated here.<sup>9</sup>

Small amounts of 4-amino-4'-chloroazobenzene (8) (10–18%) could be obtained from either 4- or 4'-chloroazobenzene (7), fluorosulfonic acid, and difluoramine. The formation of some fluorosulfate, as well as some reduction of 7 to 4-chloroazobenzene, also occurred in this reaction.



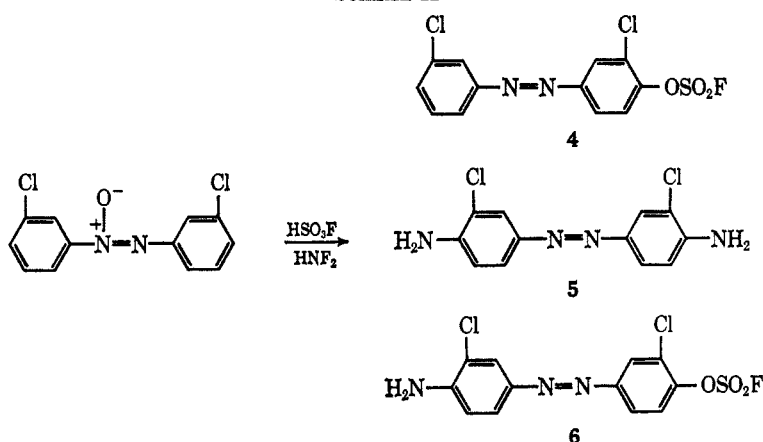
(6) (a) E. C. Buncel and B. T. Lawton, *Can. J. Chem.*, **43**, 862 (1965); (b) C. S. Hahn, K. W. Lee, and H. H. Jaffe, *J. Amer. Chem. Soc.*, **89**, 4975 (1967).

(7) (a) L. C. Behr and E. C. Hendley, *J. Org. Chem.*, **31**, 2715 (1966); (b) M. M. Shemyakin, V. I. Maimind, and T. E. Agadzhanian, *Chem. Ind. (London)*, 1223 (1961).

(8) For other pertinent discussions, see (a) P. H. Gore, *ibid.*, 191 (1959); (b) S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc., Jap.*, **36**, 601 (1963).

(9) A small amount of amination of toluene, biphenyl, and *m*-xylene by HNF<sub>2</sub>-BF<sub>3</sub>-CH<sub>2</sub>Cl<sub>2</sub> mixtures was observed. The nature of the amines produced, however, could not be determined easily; the products were complex mixtures and did not correspond to those produced in aminations with trichloroamine-aluminum chloride. See P. Kovacic and coworkers, *J. Org. Chem.*, **32**, 585 (1967), and earlier papers.

SCHEME II

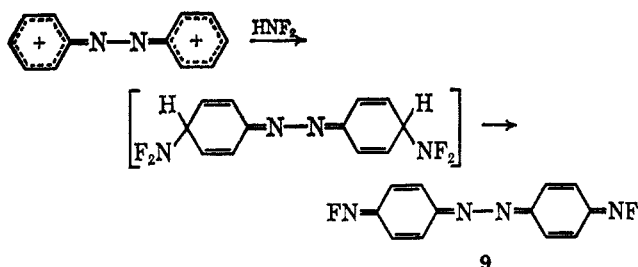


Both 4,4'-dichloro- and 4,4'-dibromoazoxybenzenes were reduced to the corresponding 4,4'-dihaloazobenzene by fluorosulfonic acid. Similar reductions were observed earlier with sulfuric acid<sup>10</sup> and chlorosulfonic acid.<sup>5</sup>

Since neither fluorosulfate **1** nor 4-aminoazobenzene is aminated by difluoramino-fluorosulfonic acid mixtures,<sup>11</sup> the unusual disubstitution products found here do not appear to arise by such an amination process.

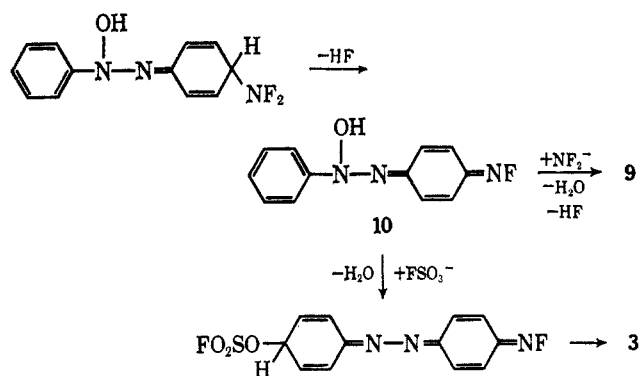
It also is unlikely that the azoxybenzene present in the reaction mixture oxidizes fluorosulfate **1** or 4-aminoazobenzene (intermolecular exchange of oxygen can apparently occur between azoxy- and azobenzenes as discussed below) to a 4-substituted azoxybenzene, which then undergoes a second Wallach reaction. Little azobenzene, the reduction product in this scheme, is isolated from these experiments, and fluorosulfate **1** and 4-aminoazobenzene were neither fluorosulfated by azoxybenzene-fluorosulfonic acid nor aminated by azoxybenzene (or 4,4'-dichloroazoxybenzene)-fluorosulfonic acid-difluoramino.

It is, of course, possible that difluoramino traps the dicarbonium ion postulated as an intermediate in the Wallach rearrangement,<sup>6</sup> and that loss of HF from the initial adduct gives **9**.<sup>12</sup> Fluorimine **9**, then, would be the material reduced to 4,4'-diaminoazobenzene.



Since disubstitution does not normally occur in the Wallach reaction, the unique nature of the difluoramino function—the potential leaving group present—may actually lead to the disubstitution products. Thus, azoxybenzene and HNF<sub>2</sub> may give an adduct that loses HF instead of H<sub>2</sub>O; an intermediate (**10**) remains

that may again undergo nucleophilic substitution to give either **9** (and eventually **2**) or the precursor to **3**.



At this time, the mechanism of these aminations must be considered obscure.

Although the intermolecular transfer of oxygen between azoxy- and azobenzenes does not explain the results of the amination with difluoramino, it appears to be the most likely cause of the small amount of 4,4'-disubstitution observed in the azoxybenzene-fluorosulfonic acid reaction. Here the azobenzene produced corresponded to the amount of disubstitution observed; so it is reasonable that azoxybenzene + **1** → azobenzene + 4-(fluorosulfato)azoxybenzene<sup>13</sup> → 4,4'-disubstituted azobenzene.

Strong support for this hypothesis was obtained when a mixture of 4,4'-dichloroazoxybenzene and azobenzene was heated with fluorosulfonic acid; a 28% yield of **1** was obtained. Undoubtedly, azobenzene was oxidized to azoxybenzene during the reduction of the dichloroazoxybenzene to 4,4'-dichloroazobenzene. The azoxybenzene would be converted into **1** under the reaction conditions. Azobenzene itself was recovered unchanged after exposure to fluorosulfonic acid at 93°. <sup>11</sup>

The presence of oxidizing material in Wallach rearrangement mixtures has been noted.<sup>7b</sup> About 25% of the theoretical active oxygen material could be titrated after 4,4'-dichloroazoxybenzene had been heated (steam bath) for 1 hr with fluorosulfonic acid. No oxygen was liberated, and the fate of the oxygen not

(10) K. Heumann, *Ber.*, **5**, 910 (1872).

(11) No fluorosulfation was observed here or in any other reactions of azobenzenes and fluorosulfonic acid.

(12) A mixed fluorosulfate-difluoramino would give rise to **3**.

(13) The 4,4'-disubstituted azobenzene actually isolated is the hydroxy fluorosulfate; the material oxidized may be 4-hydroxyazobenzene.

accounted for is not known, although oxidized organic materials may have been present.

### Experimental Section

Melting points and boiling points are not corrected.  $^{19}\text{F}$  spectra were run in carbon tetrachloride or deuteriochloroform on a Varian 4300 B spectrometer at 40 MHz;  $\phi$  values are measured in parts per million (ppm) from internal  $\text{CCl}_3\text{F}$  standard. Proton nmr spectra were recorded on a Varian A-60 spectrometer. Fluorosulfonic acid was Baker and Adamson technical grade. Methylene chloride was passed through a silica gel column. Difluoramine, a dangerous explosive,<sup>2,3</sup> must be handled with skill and caution.

**Reaction of Azoxybenzene and Fluorosulfonic Acid.**—A mixture of 10 ml of fluorosulfonic acid and 10 ml of methylene chloride was stirred at ice-bath temperature while azoxybenzene (Eastman, purified by chromatography on silica gel followed by recrystallization from hexane), 5.0 g (25.2 mmol), in 25 ml of methylene chloride was added slowly. After 1 hr at 0°, the mixture was stirred at 25° for 2 hr. The mixture was poured over ice, and the methylene chloride layer was separated and washed with water. Other runs established that no amine fraction could be isolated by further extraction of the basic aqueous layer. The residue from the methylene chloride extract was chromatographed on silica gel (G. F. Smith Chemical Co.). The column was packed in pentane, and elution was carried out with methylene chloride (2, 10, 20, 33, and 50%) in pentane, with methylene chloride, with 10% ethyl acetate in methylene chloride, and with 10% methanol in methylene chloride. The first material eluted from the column, 0.12 g, was azobenzene, identified by its infrared spectrum. The next fraction, 5.05 g (71.4%), was 4-(fluorosulfato)azobenzene (1). One recrystallization from hexane gave 4.82 g of 1, mp 96–98°; an additional recrystallization (ethanol) gave material of mp 98–100°.

Finally, 0.22 g (3%) of material, mp 102–104° (from hexane-chloroform), was eluted by methylene chloride. This presumably is 4-(fluorosulfato)-4'-hydroxyazobenzene. The  $^{19}\text{F}$  nmr spectrum had a peak at  $\phi = 38.0$ .

*Anal.* Calcd for  $\text{C}_{12}\text{H}_9\text{FN}_2\text{O}_2\text{S}$ : C, 48.6; H, 3.06; N, 9.46. Found: C, 48.8; H, 3.01; N, 9.42.

From some runs, *p*-phenylazophenol, mp and mmp 150–152°, could be obtained.

**Reaction of Azoxybenzene, Fluorosulfonic Acid, and Difluoramine.**—A mixture of 0.100 g (0.5 mmol) of azoxybenzene, 5 ml of methylene chloride, 1 ml of fluorosulfonic acid, and 112 cc (STP) (5 mmol) of difluoramine was stirred in a 25-ml sealed pressure tube<sup>14</sup> at ice-bath temperature for 1 hr and at ambient temperature overnight. The pressure tube was then vented *in vacuo* through traps cooled to –80, –110, and –196°. The –110° trap contained difluoramine, 7 cc (STP), and methylene chloride. The –196° trap contained 83 cc (STP) of (by mass spectrum) 23% difluoramine, 42% tetrafluorohydrazine, 30% silicon tetrafluoride, 2% methylene chloride, and 1% each of nitrogen, nitric oxide, and nitrous acids. Thus 26 cc (STP) of difluoramine and 35 cc (STP) of tetrafluorohydrazine was recovered. Another run of the same size under the same conditions gave 23 cc (STP) of recovered difluoramine and 33 cc (STP) of tetrafluorohydrazine. The residues from both runs were combined and poured over ice-dilute aqueous hydrochloric acid. The methylene chloride extract of the aqueous phase (both acidic and after neutralization with sodium hydroxide) was evaporated to dryness and chromatographed on silica gel with the eluents described above. In this way, 0.049 g (17.5%) of 4-(fluorosulfato)azobenzene (1) was obtained. The next fraction from the column, 0.027 g, was 4-amino-4'-(fluorosulfato)azobenzene (3), mp 171–173° dec (from hexane). The  $^{19}\text{F}$  nmr spectrum had a single peak at  $\phi = 37.2$ .

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{10}\text{FN}_2\text{O}_2\text{S}$ : C, 48.8; H, 3.41; N, 14.23. Found: C, 49.0; H, 3.33; N, 14.0.

The last fraction from the column (0.095 g, 45%) was 4,4'-diaminoazobenzene (2), mp 242–244°. The infrared spectrum was identical with that of Eastman's 4,4'-azodianiline of advertised mp 244–249°.

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{12}\text{H}_4$ : C, 67.90; H, 5.70; N, 26.41. Found: C, 67.59; H, 5.49; N, 26.08.

Another run, also conducted in duplicate, used 0.30 g (1.5 mmol) of azoxybenzene, 1 ml of  $\text{HSO}_3\text{F}$ , 5 ml of methylene chloride, and 110 cc (STP) (5 mmol) of difluoramine. The mass spectrum of the gases over the reactions indicated the following compositions: run 1, 2%  $\text{HNF}_2$ , 40%  $\text{N}_2\text{F}_4$ , 14%  $\text{CH}_2\text{Cl}_2$ , and 44%  $\text{SiF}_4$ ; run 2, 2%  $\text{HNF}_2$ , 36%  $\text{N}_2\text{F}_4$ , 28%  $\text{CH}_2\text{Cl}_2$ , and 37%  $\text{SiF}_4$ . The reactions, combined, extracted, worked up, and chromatographed as above, gave 0.312 g (37%) of 4-(fluorosulfato)azobenzene, 0.174 g (19.6%) of 4-amino-4'-(fluorosulfato)azobenzene, and 0.160 g (25%) of 4,4'-diaminoazobenzene. A third set of conditions, involving 0.50 g (2.5 mmol) of azoxybenzene, 2 ml of fluorosulfonic acid, 5 ml of methylene chloride, and 110 cc (STP) (5 mmol) of difluoramine, gave 55% 4-(fluorosulfato)azobenzene, 5% 4-amino-4'-(fluorosulfato)azobenzene, and 15.6% 4,4'-diaminoazobenzene.

**Reaction of 3,3'-Dichloroazoxybenzene, Fluorosulfonic Acid, and Difluoramine.**—A mixture of 0.27 g (1 mmol) of 3,3'-dichloroazoxybenzene, 1 ml of fluorosulfonic acid, 3 ml of methylene chloride, and 110 cc (STP) of difluoramine in the 25-ml pressure tube<sup>14</sup> was stirred 1 hr at 0° and overnight at ambient temperature. The gas over the reaction mixture, by mass spectrum, was 7%  $\text{HNF}_2$ , 43%  $\text{N}_2\text{F}_4$ , 20%  $\text{CH}_2\text{Cl}_2$ , and 30%  $\text{SiF}_4$ . The reaction residue was poured over ice and worked up as described above. Chromatography of the organic material over silica gel gave 0.138 g (39.5%) of 3,3'-dichloro-4-(fluorosulfato)azobenzene (4) (Table I) and 0.053 g (18.7%) of 3,3'-dichloro-4-amino-4'-(fluorosulfato)azobenzene (6), mp 115–116° (from hexane). The  $^{19}\text{F}$  nmr spectrum had a singlet peak at  $\phi = 41.1$ .

*Anal.* Calcd for  $\text{C}_{12}\text{H}_8\text{Cl}_2\text{FN}_2\text{O}_2\text{S}$ : C, 39.6; H, 2.21; N, 11.5. Found: C, 39.8; H, 2.32; N, 11.3.

The last fraction eluted from the column was 4,4'-diamino-3,3'-dichloroazobenzene (5): yield, 0.145 g (39.0%); mp 215–217° (from methanol).

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_4$ : C, 51.26; H, 3.59; N, 19.93; Cl, 25.22. Found: C, 50.8; H, 3.38; N, 19.5; Cl, 25.8.

When the reaction was conducted under the same conditions using 0.54 g (2 mmol) of 3,3'-dichloroazoxybenzene, 1 ml of fluorosulfonic acid, 4 ml of methylene chloride, and 160 cc (STP) of difluoramine, 0.34 g (48.5%) of 4, 0.135 g (18.5%) of 6, and 0.162 g (22%) of 5 were isolated. The gases from the reaction mixture, trapped *in vacuo* in –110 and –196° traps, contained 30 cc of difluoramine and 49 cc of tetrafluorohydrazine.

A third run under the same conditions with 0.27 g of azoxy compound, 1 ml of fluorosulfonic acid, 4 ml of methylene chloride, and 160 cc (STP) of difluoramine gave 0.094 g (27%) of 4, 0.037 g (13%) of 6, and 0.101 g (28%) of 5.

**Reaction of 4'-Chloroazoxybenzene (7), Fluorosulfonic Acid, and Difluoramine.**—A mixture of 0.47 g (2 mmol) of 4'-chloroazoxybenzene, 1 ml of fluorosulfonic acid, 5 ml of methylene chloride, and 160 cc (STP) of difluoramine was stirred overnight at ambient temperature. A total of 25 cc of difluoramine and 52 cc (STP) of tetrafluorohydrazine was obtained from the volatile gases in the tube. The organic residue, after the usual aqueous work-up, was chromatographed on silica gel. The first fraction isolated was 4-chloroazobenzene (0.039 g) identified by infrared spectrum. After this came 0.082 g of a mixture of 4-chloroazobenzene and 4-chloro-4'-(fluorosulfato)azobenzene and 0.033 g of clean 4-chloro-4'-(fluorosulfato)azobenzene. The next fraction was 4-amino-4'-chloroazobenzene (0.127 g, 18%), mp 148–150° from hexane (lit.<sup>15</sup> mp 147–148°).<sup>15</sup> The infrared spectrum of this material was identical with that of an authentic sample prepared from 4-chloronitrosobenzene and *p*-phenylenediamine.

*Anal.* Calcd for  $\text{C}_{12}\text{H}_9\text{ClN}_2$ : C, 62.2; H, 4.35; N, 18.14; Cl, 15.3. Found: C, 61.8; H, 4.34; N, 18.20; Cl, 14.9.

**Reaction of Fluorosulfonic Acid, 4,4'-Dichloroazoxybenzene, and Azobenzene.**—A mixture of 2.67 g (10 mmol) of 4,4'-dichloroazobenzene, 2.73 g (15 mmol) of azobenzene, and 20 ml of fluorosulfonic acid was heated on a steam bath for 1 hr. The mixture was cooled, poured over ice, and extracted with methylene chloride. The methylene chloride solution was washed with water and 10% aqueous sodium bicarbonate solution. The residue left by evaporation of the methylene chloride was chromatographed on silica gel; 5% methylene chloride in pentane was inserted into the usual list of eluents. The initial fractions contained a mixture

(15) L. von Mechel and H. Stauffer. *Helv. Chim. Acta*, **24**, 151 (1941); *Chem. Abstr.*, **36**, 6808 (1941).

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

of azobenzene and 4,4'-dichloroazobenzene; these were not weighed or characterized. The next fraction (0.785 g, 28%) was 4-(fluorosulfato)azobenzene (1), crude mp 96–99° (mixture melting point with 1 from azoxybenzene was 97–99°). The infrared spectrum was identical with that of earlier samples of 1.

**Registry No.**—Fluorosulfonic acid, 7789-21-1; fluorosulfonic acid-difluoramine, 16704-22-6; 1, 16704-23-7; 4-(fluorosulfato)-4'-hydroxyazobenzene, 16704-24-8; 3, 16704-25-9; 5, 16704-26-0; 6, 16704-27-1.

## Syntheses and Reactions of Triarylsulfonium Halides<sup>1</sup>

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Triarylsulfonium halides have been prepared by the reaction of diaryl sulfoxides with aromatic hydrocarbons in the presence of a large excess of aluminum halide. The structures of the salts were established by pyrolysis and subsequent glpc analysis of the pyrolysates. On the basis of product ratios produced in the pyrolysis reactions, it was possible to suggest what seemed to be the most plausible mechanism of thermal decomposition of the salts. The reaction of diphenyl-*p*-tolylsulfonium bromide with sodium *t*-butoxide was also investigated. The formation of acetone and a host of other products indicated the operation, at least in part, of a radical reaction in this instance.

In order to investigate the effects of substituents on the reactions of triarylsulfonium halides, it was first necessary to develop a reliable method of synthesis of such salts. One method that seemed potentially useful was that of Wildi, Taylor, and Potratz,<sup>2</sup> who prepared triphenylsulfonium bromide by treatment of diphenyl sulfoxide with phenylmagnesium bromide. However, when an attempt was made to prepare phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium bromide by causing phenyl *p*-tolyl sulfoxide to react with 2,5-dimethylphenylmagnesium bromide in benzene at 75°, no reaction occurred. This was probably due in part to the sterically hindered nature of the Grignard reagent. However, it was also found that no product was obtained when *p*-anisyl- or *p*-bromophenylmagnesium bromide was used. Also, aryllithiums are known not to give appreciable quantities of sulfonium salts when caused to react with diaryl sulfoxides.<sup>3</sup>

Another route that appeared promising was the treatment of a diaryl sulfide with a diazonium compound, as had been developed by Horner and Hoffmann<sup>4</sup> in their synthesis of tetraarylphosphonium salts. However, treatment of diphenyl sulfide with benzenediazonium chloride or *p*-toluenediazonium tetrafluoroborate produced no sulfonium compounds, even when cuprous chloride was added as a catalyst.

Courtout and Tung<sup>5</sup> have reported the syntheses of phenyl-*p*-tolyl-2,3-dimethylphenyl- and phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium chlorides by the reaction of phenyl *p*-tolyl sulfoxide with *o*- and *p*-xylene, respectively, in the presence of aluminum chloride at 40°. Our attempts to reproduce their results met with failure.

Finally, the desired sulfonium salts were prepared by using the method of Courtout and Tung<sup>5</sup> in a drastically modified form. Excess aluminum chloride and much higher reaction temperatures were found necessary to promote formation of the sulfonium salts. About a sixfold molar excess of aluminum chloride was found to

work best, although the reason for this is not understood at this time. The most suitable reaction temperature was the reflux temperature of the aromatic hydrocarbon employed in excess as reactant and solvent. Aluminum bromide was also found suitable for use in this reaction, especially in preparation of the bromide salts. By use of this method, several asymmetric and a number of other triarylsulfonium salts were prepared in good yield and purity.

When benzene was employed as a reagent, the synthesis was unambiguous. However, because of the high reaction temperatures involved, a possible aluminum chloride induced migration of the methyl groups on the methyl-substituted benzenes was a possibility to be considered. Use of toluene or *m*-xylene also opened up possibilities of product mixtures arising from electrophilic substitution at various positions on the hydrocarbon in question. In practice, however, as demonstrated by pyrolysis studies to be described later, almost exclusive *para* substitution occurred with toluene, while *m*-xylene yielded exclusively the diaryl-2,4-dimethylphenylsulfonium salt. The results of these syntheses are summarized in Table I.

The melting point of phenyl-*p*-tolyl-2,5-dimethylphenylsulfonium chloride, as noted in Table I, also brings the results of Courtout and Tung<sup>5</sup> into question. The melting point of this anhydrous salt was found by us to be 122–123°, whereas the French authors reported a value of 73–74°. This latter figure is quite close to that observed for the starting material, phenyl *p*-tolyl sulfoxide, mp 75–76°. Phenyl-*p*-tolyl-2,3-dimethylphenylsulfonium chloride, as obtained by these same workers, is reported to have a melting point of 74–76°, almost the same as that for phenyl *p*-tolyl sulfoxide. In our attempts to reproduce the results of Courtout and Tung,<sup>5</sup> we recovered at least a significant portion of the sulfoxides unchanged.

It is of practical value and theoretical interest that triarylsulfonium halides undergo pyrolysis at moderate temperatures to produce theoretical yields of diaryl sulfides and the corresponding aryl halides. ( $R_3S^+ + X^- \rightarrow RX + R_2S$ ). The practical value lies in the fact that the products of pyrolysis are easily analyzed by vapor phase chromatography, and this constitutes the most convenient method for determining

(1) A preliminary report of this work has been published: G. H. Wiegand and W. E. McEwen, *Tetrahedron Lett.*, 2639 (1965).

(2) B. S. Wildi, S. W. Taylor, and H. A. Potratz, *J. Amer. Chem. Soc.*, **73**, 1965 (1961).

(3) K. K. Anderson and S. A. Yeager, *J. Org. Chem.*, **28**, 865 (1963).

(4) L. Horner and H. Hoffmann, *Ber.*, **91**, 45 (1958).

(5) C. Courtout and T. Y. Tung, *Compt. Rend.*, **197**, 1227 (1933).