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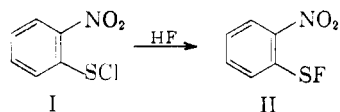
Derivatives of Sulfenic Acids. XXIX. Bis(2,2'-fluorosulfonyl)azobenzene via 2-Nitrobenzenesulfonyl Chloride and Hydrogen Fluoride¹

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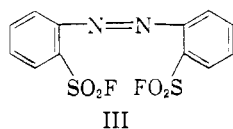
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The reaction of 2-nitrobenzenesulfonyl chloride (I) with liquid hydrogen fluoride was studied as a possible route to 2-nitrobenzenesulfonyl fluoride (II). Besides tars, and a small amount of an unidentified, colorless product (found when carbon tetrachloride was used as diluent), there was formed 5–15% of the bright-red bis(2,2'-fluorosulfonyl)azobenzene, III. The proof of structure of III is given and related preparative details are reported.

Introduction. Concurrently with attempts to prepare 2,4-dinitrobenzenesulfonyl fluoride and *p*-toluenesulfonyl fluoride,² reaction 1 was studied as a possible route to 2-nitrobenzenesulfonyl fluoride, II. It was found that I and liquid hydro-



gen fluoride react vigorously,³ but none of the desired sulfonyl fluoride could be found. Besides much tar, there was also formed a crystalline, bright-red solid, whose structure was not immediately apparent to us, but which now has been shown to be bis(2,2'-fluorosulfonyl)azobenzene, III.



The yield of III seems not to depend greatly on the conditions of the reaction, ranging from 5 to 15% by working in liquid hydrogen fluoride at

–70°, 0°, or room temperature, or in the presence or absence of organic solvents.⁴ In our experience, the most convenient procedure is to work at –70°, using a polyethylene flask, magnetic stirrer, and without adding an organic solvent.

Evidence for structure III. Since the elementary analysis (C,H,N,S,F) for the red compound agreed for 2-nitrobenzenesulfonyl fluoride (II), it was first considered [Cf. footnote 3 of ref. (2)] that this might be the structure of the product. Further study of its physical properties, such as solubility and spectra, and an initial study of its chemical properties, however, showed that the new fluorine compound was distinct from the sulfonyl chloride (I) or the corresponding sulfonyl bromide (*o*-NO₂-C₆H₄SBr), which resemble each other closely. Furthermore, although the low solubility of the new fluorine compound made determination of the molecular weight difficult, the molecular weight (Rast method, in camphor) indicated a dimeric structure, whereas the sulfonyl fluoride would not be expected to be a dimer.⁵ Structure II was therefore ruled out of consideration.

The azo structure for III was foreshadowed by the observation that the red fluoride added hydrogen (H₂, Raney nickel) to form a colorless product that was suspected to be a hydrazo compound. Since an azo group could also be responsible for the observed color, and because there was some precedent for oxidation-reduction reactions between the bivalent sulfur moiety of sulfonyl deriv-

(1) We are indebted to Research Corporation for a grant which permitted initiation of this project. The study was completed under sponsorship of the United States Office of Scientific Research, Air Research and Development Command (Project OSR-30-19). It is published for technical information only and does not necessarily represent recommendations or conclusions of the sponsoring agency. For references to earlier papers of this series, Cf. Part XXVI, *J. Chem. Ed.*, **33**, 585 (1956) and *J. Org. Chem.*, **22**, 1673, 1701 (1957).

(2) D. L. Chamberlain and N. Kharasch, *J. Am. Chem. Soc.*, **77**, 1041 (1955). As recorded in this reference, all attempts, to date, to synthesize sulfonyl fluorides have failed, with the possible exception of CF₃-(CF₂)₁₁-SF, which is claimed in U. S. Patent 2,519,983, but no supporting data for the structure of the product are given [cf. *Chem. Abstr.*, **45**, 51 (1951)].

(3) H. J. Emeleus and H. G. Heal, *J. Chem. Soc.*, 1126 (1946), recorded that there was no reaction in this instance. With other aromatic sulfonyl chlorides, however, they observed extensive reactions, giving tars, disulfides (in some cases), and higher fluorides. The latter were presumed to arise through disproportionations of the initially formed sulfonyl fluorides, ArSF.

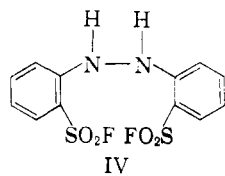
(4) When carbon tetrachloride was used as a diluent for the reaction, a small amount of an unidentified, colorless, low-melting solid (cf. experimental) was also observed. This product has also been noted by H. H. Szmant, who had occasion to carry out the reaction of 2-nitrobenzenesulfonyl chloride and liquid hydrogen fluoride, using carbon tetrachloride as diluent (private communication from H. H. S. to N. K.). An investigation of this product is being made in this laboratory.

(5) In the absence of conclusive evidence, the possibilities of structures as ArS(Cl)-S(Cl)Ar, for the products of reaction of chlorine with bis(aryl) disulfides had to be considered. However, in the case of 2,4-dinitrobenzenesulfonyl chloride, *e.g.*, the molecular weight was 234.6 (found, by the cryoscopic method, in benzene; *vs.* 234 calcd. for the monomer). Cf. N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2726 (1949).

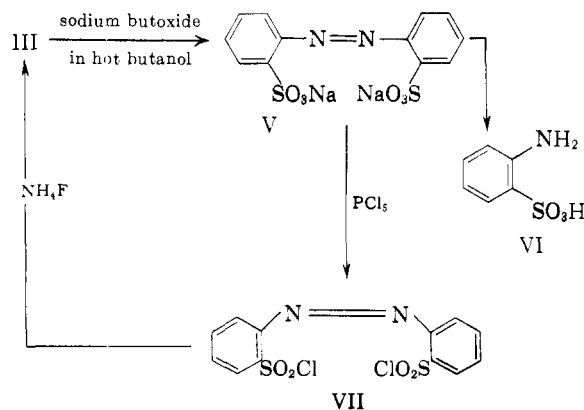
atives and adjacent nitro groups,⁶ it appeared that the reaction of 2-nitrobenzenesulfonyl chloride with liquid hydrogen fluoride might involve a novel conversion, leading to a structure like III. That III is, indeed, the structure of the product was then confirmed as follows.

(1) Fig. 1 shows the ultraviolet absorption spectra of azobenzene, the new fluoride (hereafter referred to as III) and bis(2,2'-chlorosulfonyl)azobenzene.⁷ The near identity of all three curves leaves little doubt, if any, that an azo group must be present in the new fluoride compound. For comparison, the spectra of 2-nitrobenzenesulfonyl chloride and 2-nitrobenzenesulfonyl bromide are also shown in Fig. 1.

(2) The derivative obtained by hydrogenation (as mentioned above) was also obtained by reducing III by various methods, *e.g.* with stannous chloride. On oxidation, even by exposure to air, the colorless reduction product readily reverted to III. Since we conclude that III is the correct structure of the red compound, IV is the logical one for the product of reduction.



(3) Under severe solvolytic conditions (treatment with a solution of sodium *n*-butoxide, in *n*-butyl alcohol, at reflux) III gave a red water-soluble sodium salt, V, which was characterized as the di(*S*-benzylthiuronium) salt, m.p. 228–229°. The *ortho* relation of the azo and sulfonate functions in V was then confirmed by catalytic reduction to orthanilic acid (VI). Compound V was also converted to VII; and original III was obtained from



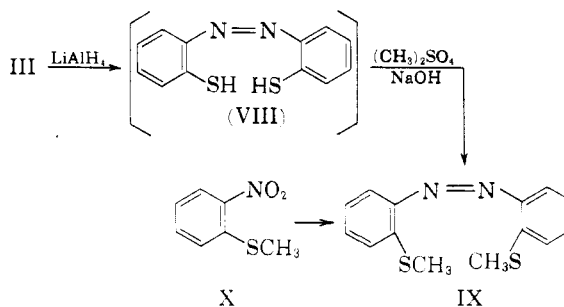
(6) The conversion of 2-nitrobenzenesulfonyl chloride to orthanilic acid was observed by Zincke and Farr, *Ann.*, **391**, 55 (1912). Similarly, Kharasch, King, and Bruce found that methyl 2,4-dinitrobenzenesulfonate, may be converted, by treatment with hot hydrochloric acid solutions, to 2-amino-4-nitrobenzenesulfonic acid.

(7) The preparation of this compound is described further in the text and in the experimental part.

VII by reaction with ammonium fluoride in acetone.

Since no rearrangement of V is expected under alkaline conditions, the cycle of reactions, III→V→VII→III, confirms that the only change effected in the reaction of III with sodium butoxide is conversion of -SO₂F to -SO₂ONa. Fairly drastic conditions were required for the hydrolysis of the fluorosulfonyl groups, as anticipated for III on the basis of the known hydrolytic stabilities of sulfonyl fluorides.⁸ The inertness of III to solvolytic reactions is further illustrated below.

(4) Alkaline reduction of 3-nitrobenzenesulfonic acid is known to yield the salts of the bis-3,3'-azobenzenedisulfonic acid.⁹ While we confirmed this conversion, the extension to the similar synthesis of V, from *o*-nitrobenzenesulfonic acid, could not be effected. Because of this failure to achieve the independent synthesis of V, the sequence of reactions, III→IX, as well as the alternate synthesis of IX from X, by the recorded method of Brand¹⁰ were carried out. These reactions confirm the presence of an azo group in III and also show that it is situated *ortho* to the sulfur function.



Compound VIII was not isolated, as such, but was methylated directly to IX.

(5) The infrared spectra of the fluoride, III, and of azobenzene were examined. The most striking feature of the spectrum of the fluoride is the presence of two strong bands, at 1209 cm.⁻¹ and 1394 cm.⁻¹, which are absent in the spectrum of azobenzene. These are the sulfone bands, which generally occur¹¹ at 1120–1160 cm.⁻¹ and 1350–1400 cm.⁻¹, and which are known, from the Raman spectra, to occur in sulfonyl fluorides¹² at 1167–1197 cm.⁻¹ and at 1402–1412 cm.⁻¹ The assignment of infrared absorptions for the azo group has not yet been made with sufficient assurance;¹³ hence, no conclusion as to the presence

(8) J. Simons, *Fluorine Chemistry*, Vol. I, Academic Press, New York, N. Y. (1950), p. 178.

(9) Dr. Mahrenholtz and Dr. Gilbert, *Ann.*, **202**, 331 (1880); cf. also, S. Stern and A. Taub, *J. Am. Pharm. Assoc.*, **28**, 1032 (1939); and H. Limpricht, *Ber.*, **11**, 1046 (1878).

(10) K. Brand, *Ber.*, **42**, 3463 (1909).

(11) R. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., 1954, p. 279.

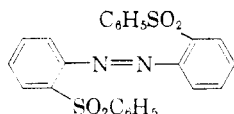
(12) N. S. Ham and A. M. Hamble, *Australian J. Chem.*, **6**, 135 (1953).

(13) R. J. W. Le Fevre, M. F. O'Dwyer, and R. L. Werner, *Australian J. Chem.*, **6**, 341 (1953).

of this group was drawn from the infrared spectrogram.

A few other points related to III are noted below. (a) Bis(2,2'-fluorosulfonylazobenzene) is a very stable substance. It sublimes, without decomposing, near its melting point (259–260°, uncorr.), is completely inert to water and mineral acids, and may be recrystallized, without loss, from hot concentrated nitric acid. It is not affected by bromine and does not react with sodium sand, in refluxing toluene. Treatments of III with cold chromic acid, cold sulfuric acid, or potassium permanganate are also without effect; but hot sulfuric acid or hot mixtures of nitric and sulfuric acids, attack III. Similarly, solvolysis of the fluoride does not occur appreciably by attempted reactions with boiling methanol, aniline, and several other nucleophilic reagents. It dissolves only with difficulty, without reacting, in a large volume of boiling acetone, from which it crystallizes (on rapid cooling) in fine, orange needles, m.p. 256–257° (uncorr.); or, on slow cooling, in heavy, deep-red cubes (1–2 mm. in length), which melt somewhat higher (258–259° and 259–260°, both melting points having been observed on different samples). The inability of the several powerful oxidants, mentioned above, to attack the azo linkage reflects a lowered reactivity of this azo group, compared to other azo compounds. This is probably related mainly to the powerful electron-withdrawing effect of the *ortho*-fluorosulfonyl groups in III.

(b) Treatment of III with benzene and boron trifluoride, under Friedel-Crafts conditions, gave only unreacted III; but with aluminum chloride as catalyst, the corresponding bis(2,2'-benzenesulfonyl)azobenzene, XII, was obtained. The as-



signment of structure XI is based on analysis, mode of synthesis and the ultraviolet spectrum and makes the reasonable assumption that no rearrangement of the substituent $-SO_2F$ groups occurs in the conversion to XI. It is likely that the chloride, VII, corresponding to III, is an intermediate in the synthesis of XI, since the reactions of sulfonyl fluorides with aluminum chloride¹⁴ are known to give sulfonyl chlorides. From steric considerations, the *trans* structure of XI can scarcely be doubted. On empirical grounds, also, there is little doubt that all the azo compounds reported in this paper are the *trans* isomers, but their geometry has not been established independently.

EXPERIMENTAL¹⁵

Synthesis of bis(2,2'-fluorosulfonyl)azobenzene, III. A 500-

(14) M. W. Renoll, *J. Am. Chem. Soc.*, **64**, 1489 (1942).

(15) Melting points are not corrected; they were made in glass capillaries, in a liquid bath.

ml. polyethylene bottle, fitted with a magnetic stirrer and cooled in an acetone-solid carbon dioxide bath was placed in a good hood. Hydrogen fluoride (200 ml.) was added and to this was introduced 11.0 g. (0.06 mole) of powdered 2-nitrobenzenesulfonyl chloride. The yellow suspension turned red as the reaction mixture was warmed to room temperature. After standing about 12 hr., to vent the hydrogen fluoride, the black, semi-solid residue was extracted with cold acetone. Evaporation of the extracts gave magnificent red needles of the fluoride (0.5 g.), m.p. 259–260°. Further extraction of the black tar with hot acetone, using chromatographic or crystallizing procedures, failed to yield any identifiable material. Since the red fluoride (III) was inert to concentrated nitric acid, an attempt to "burn off" the impurities by boiling with nitric acid was made, but no additional III was obtained.

The preparation was repeated several times, using up to 160 g. (0.84 mole) of I. The yield of III was 14.5 g. (10.6% yield), from 160 g. of the sulfonyl chloride and the yields in various runs were from 5% to 15%, based on 2 moles I \rightarrow 1 mole III.

Anal. Calcd. for $C_{12}H_8O_4F_2N_2S_2$: C, 41.61; H, 2.33; F, 10.97; N, 8.09; S, 18.52; mol. wt., 346. Found (on different samples, in different analytical laboratories): C, 41.38, 41.71, 42.40; H, 2.45, 2.54, 1.97; F, 9.61, 9.44, 10.50; N, 8.42, 8.76; S, 18.29, 18.54. Mol. wt. (Rast method, in camphor): 333.

The product (III) was too insoluble in convenient solvents to permit determination of the molecular weight by usual cryoscopic or isothermal (Signer) methods.

With carbon tetrachloride as a diluent in the above reactions, III resulted in low yield and a white, waxy product of low melting point was also found. Thus: Hydrogen fluoride (100 ml.), forming the upper layer, was added to 100 ml. of carbon tetrachloride. The mixture was stirred in a polyethylene flask, at room temperature and a solution of I (5 g., 0.025 mole in 100 ml. carbon tetrachloride) was added. As judged through the opaque flask, the carbon tetrachloride layer appeared cream colored, the interface was green, and the hydrogen fluoride layer was violet. The hydrogen fluoride was evaporated overnight and its removal completed with a stream of nitrogen.

The carbon tetrachloride layer and a red, oily solid were then homogenized by adding acetone, the solution was treated with charcoal and the solvents were removed *in vacuo* until only 25 ml. of solution remained. On cooling, the mass set to a semi-solid and was extracted with low-boiling petroleum ether, leaving a 100 mg. residue of III. Evaporation of the petroleum ether solution yielded a white, waxy solid, m.p. 55–57°, apparently identical with the product described by Szmant (*cf.* footnote 4).

An attempted reaction with nitromethane as solvent gave no III. The attempt to prepare III, using 48% hydrogen fluoride, also failed. Instead, hydrolysis products of I (the disulfide and thiosulfonate ester) were encountered.

Bis(2,2'-fluorosulfonyl)azobenzene is insoluble in ether, and almost completely insoluble in benzene, ethylene chloride, and chloroform. It is moderately soluble in hot acetone, ethyl acetate, and pyridine and quite soluble in *N,N*-dimethylformamide. Crystallization from a large volume of acetone, with rapid cooling, gave fine orange needles of III. Slow or spontaneous crystallization from hot acetone gave deep-red rectangular crystals, 1–1.5 cm. long and 1–2 mm. wide. The melting point varied slightly with the crystal form; the orange crystals melted at 256–257° and the larger red crystals at 258–259°.

The ultraviolet spectra of 2-nitrobenzenesulfonyl chloride (I) and the corresponding bromide were determined in purified dioxane¹⁶ and that of III was made in dioxane, as well as in ethylene chloride, using a Beckmann DU quartz

(16) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Organic Compounds*, John Wiley and Sons, New York, N. Y., 1951, p. 12.

spectrophotometer. The ultraviolet spectra of VII, bis(2,2'-chlorosulfonyl)azobenzene and of azobenzene were determined in ethylene chloride. The ultraviolet spectra of the sulfonyl chloride, I, the corresponding bromide, and III were also determined in concentrated sulfuric acid, but the spectra varied with time and are not recorded here. The infrared spectrum of I was obtained on a Nujol mull, with a Perkin-Elmer double beam instrument.

Reduction of III to bis-2,2'-fluorosulfonylhydrazobenzene, IV. The fluoride, III, 500 mg., was dissolved in 100 ml. of absolute ethanol, about 1 g. of Raney nickel catalyst was added, and the mixture shaken with hydrogen at 45 p.s.i. for 2 hr. The Raney nickel was separated and the colorless filtrate was concentrated, cooled, and the crystals collected. Recrystallization from 95% ethanol gave excellent white crystals of IV, m.p. 156–157°.

Anal. Calcd. for $C_{12}H_{10}O_4F_2N_2S_2$: C, 41.38; H, 2.87; N, 8.04; S, 18.30. Found: C, 41.77; H, 3.18; N, 7.81. On a different sample: C, 41.83; H, 2.84; N, 8.26.

On standing in the open air for extended periods, or on treatment with dilute nitric acid at room temperature, the reduced compound (assigned structure IV) quantitatively reverted to III.

*Treatment of III with sodium *n*-butoxide in *n*-butyl alcohol.* III (1.0 g.) was added to a cold solution of 400 mg. of sodium in *n*-butyl alcohol (30 ml.). The resulting red solution was boiled for 30 min., during which time a red-orange precipitate formed. This was collected (1.150 g. crude material). The red product was very soluble in cold water. Acidification of the solution caused no precipitate to form nor was a change in color noted with change of pH. The product was completely insoluble in nonpolar solvents and could be purified only with difficulty from a large volume of absolute ethanol. The latter treatment removed a buff-colored solid and gave a yellow-orange powder, presumed to be the still somewhat impure and possibly solvated disodium salt of V.

Anal. Calcd. for $C_{12}H_8O_6N_2Na_2S_2$ (V): C, 37.31; H, 2.07; N, 7.25; S, 16.53; Na, 11.92. Found: C, 37.20; H, 4.2; N, 6.85; S, 15.83; Na, 11.10.

The red sodium salt darkened and decomposed at 290–310° and left a residue on ignition. To characterize the product more fully, the neutral aqueous solution of the sodium salt was treated with a cold aqueous solution of *S*-benzylthiuronium chloride. The resulting orange precipitate was crystallized from hot water and from aqueous methanol, giving a product which melted at 228–229°. Melting was accompanied by decomposition to a black oil.

Anal. Calcd. for the di-*S*-benzylthiuronium salt of 2,2'-azobenzenedisulfonic acid, $C_{28}H_{30}O_6N_6S_4$: C, 49.55; H, 4.6; N, 12.46; S, 19.0. Found: C, 49.54; H, 4.62; N, 12.46; S, 18.0.

Treatment of the acidified, aqueous solution of the disodium salt of V with zinc metal gave a colorless solution; and diazotization of this solution, then coupling with alkaline β -naphthol, gave a deep red dye, which was not investigated further. Presumably, the dye stems from orthanilic acid (see below).

Conversion of V to the disulfonyl chloride (VII). The orange disodium salt (V), 830 mg., was triturated with 1.0 g. of phosphorus pentachloride. The excess phosphorus pentachloride was hydrolyzed with water and the organic material was extracted with benzene. The benzene extract was passed through a column of silica and the first fractions eluted from the column were evaporated, giving a solid, which was recrystallized from a mixture of benzene and low-boiling petroleum ether. The product, 400 mg. was lavender in color and melted at 167–168°.

Anal. Calcd. for $C_{12}H_8O_2Cl_2N_2S_2$ (VII): C, 38.0; H, 2.10; N, 7.37; Cl, 18.68. Found: C, 39.15; H, 2.18; N, 7.20; Cl, 17.23.

Treatment of a small quantity of VII with ammonium fluoride, in acetone, gave a product which corresponded (m.p. and spectra) to III, thus completing the cycle III \rightarrow V \rightarrow VII \rightarrow III.

Reduction of the disodium salt, V, to orthanilic acid, VI. The disodium salt, V, 600 mg., was dissolved in 50 ml. of water. About 500 mg. of Raney nickel catalyst was added and the mixture shaken with hydrogen at 45 p.s.i. for 2 hr. The colorless solution was separated from the catalyst and the filtrate was concentrated to 10 ml. and acidified with hydrochloric acid, causing precipitation of a white product (200 mg.). Treatment of the latter with diethylamine gave the diethylammonium salt of orthanilic acid, m.p. 177–178°. There was no depression of melting point on admixture of an authentic specimen of the salt, which melted at 176–178°, and is recorded¹⁷ to melt at 177–178°.

Repetition of the reduction, using 700 mg. of salt V, gave 250 mg. of free orthanilic acid (characterized as the diethylammonium salt).

Bis(2,2'-methylmercapto)azobenzene, IX. To prepare methyl 2-nitrophenyl sulfide (X), bis(2-nitrophenyl)disulfide (13 g., 0.04 mole)¹⁸ was refluxed for 30 min. with a soln. prepared from 5.6 g. (0.02 mole) of sodium sulfide nonahydrate and 4 g. (0.1 mole) of sodium hydroxide, in 45 ml. of 95% ethanol and 25 ml. of water. The dark reaction mixture was diluted with water (100 ml.), filtered, warmed to 45° and shaken with dimethyl sulfate (10 g., 0.08 mole). After cooling, the precipitated methyl 2-nitrophenyl sulfide (7.3 g., 0.04 mole) was collected and crystallized from 95% ethanol. It melted at 87° (lit.,¹⁹ 85–87°).

Conversion of methyl 2-nitrophenyl sulfide (X) to IX. To a refluxing solution of X (1.5 g., 0.09 mole), in 20 ml. 95% ethanol, was added a solution of 1.5 g. sodium hydroxide in 5 ml. water. Zinc dust (2.6 g.) was added in portions to the hot solution and the mixture refluxed 15 min. Filtration and cooling of the filtrate gave a first crop of red product, and concentration of the mother liquor gave more product. The combined crude products were taken up in 95% ethanol (100 ml.), the solution filtered to remove zinc salts and the filtrate concentrated to give IX (830 mg., 0.006 mole), m.p. 155° (lit.¹⁰ 156–158°).

To confirm the structure of IX, it was cleaved with sodamide to the disodium salt of VIII and remethylated to IX. Compound IX (1.0 g.) was added to a solution of sodamide, prepared from 1.0 g. sodium and 150 ml. of liquid ammonia, and the ammonia was evaporated. The residue was treated with water, to give a violet-red aqueous extract, and a residual orange solid. The latter was insoluble in carbon tetrachloride, ethyl acetate, and acetone and is presumably a polymeric disulfide of VIII, formed by partial oxidation. The violet-red solution and orange residue were refluxed with 1.0 g. of sodium sulfide nonahydrate for 30 min. and the mixture was diluted with water and filtered, to give a small amount of solid residue and a deep red filtrate. The latter was warmed to 50° and shaken with 1.0 g. of dimethyl sulfate. An orange emulsion formed immediately, and on cooling there precipitated 0.06 g. of IX, m.p. and mixture m.p. with IX (made alternately, as above) 155°. The above procedure was patterned on the work of Hughes and Thompson.¹⁹

Conversion of III to IX. Bis(2,2'-fluorosulfonyl)azobenzene, 700 mg., was added to a refluxing slurry of lithium aluminum hydride (1.0 g.) in 250 ml. of ether. A colorless solution was obtained after 1 hr., but it was noted that a pink color developed on cooling and that this color change was reversible with heating and cooling. Treatment of the alkaline reaction mixture with water and dilute sulfuric acid gave a yellow precipitate. This was extracted from the acidic solution with ether, leaving a trace of a greenish solid, and forming a red ethereal solution. The ethereal solution was shaken with 50 ml. of 10% aqueous sodium hydroxide

(17) S. Morita and M. Sugahara, *J. Chem. Soc., Japan, Pure Chem. Sect.*, **72**, 621–623 (1951). *Chem. Abstr.*, **46**, 6039 (1952).

(18) *Org. Syntheses, Coll. Vol. I*, 220 (1941).

(19) Hughes and Thompson, *Proc. Royal Soc. New South Wales*, **83**, 269 (1949).

solution, to give a deep purple aqueous layer and a colorless ethereal solution. To assure complete reduction, the aqueous purple layer was refluxed, as in the preceding experiment, with sodium sulfide nonahydrate (1.0 g.) for 30 min. The deep red solution which resulted was shaken, at 50°, with 1.0 g. of dimethyl sulfate. The cooled solution gave ca. 50 mg. of a pale-orange material, which still contained a trace of inorganic salts, for it did not melt completely, even at 290°. Recrystallization from ethylene chloride removed the colorless, inorganic impurity and left bis(2,2'-methylmercapto)azobenzene, m.p. and mixture m.p. with an authentic specimen,¹⁰ 154–155°. The remaining material from the reduction of III was present as a water soluble compound and was not examined.

Synthesis and characterization of 3,3'-azobenzenedisulfonic acid. *m*-Nitrobenzenesulfonyl chloride (22 g., 0.1 mole) was refluxed with a solution of potassium hydroxide (28 g., 0.5 mole) in 240 ml. water, to give a clear yellow solution. Stirring and refluxing for 2 hr., while portions of zinc dust were added, gave a clear, colorless solution, from which the excess zinc was removed by filtration. The filtrate was refluxed for 2 hr., while a stream of air was passed through the solution, whereby a deep red solution resulted. The dissolved zinc salts were precipitated as the carbonates, by adding carbon dioxide, and the precipitate was collected. The red filtrate was evaporated, yielding the crude orange-red potassium salt (14.3 g.). Two recrystallizations from water gave an analytical sample.

Anal. Calcd. for $C_{12}H_5O_6K_2N_2S_2$: C, 34.28; H, 1.90; N, 6.67; S, 15.24; K, 18.57. Found: C, 33.90; H, 2.37; N, 6.92; S, 15.48; K, 18.30.

Reduction of the water solution of the potassium salt with hydrogen and Raney nickel, at 45 p.s.i., gave a colorless solution which, on concentration and acidification, gave a white precipitate. The diethylammonium salt of the latter melted at 143–145°, without purification. The reported melting point of the diethylammonium salt of metanilic acid is 148°.⁷

To assure the structure of the above salt it was converted to a series of derivatives, as follows:

Bis(3,3'-azobenzene)disulfonic acid (potassium salt), 1.0 g., was mixed with 1.0 g. phosphorus pentachloride and the mixture warmed several minutes. After hydrolysis of the excess phosphorus pentachloride, the red precipitate was recrystallized from methyl acetate and low-boiling petroleum ether mixture. The product melted at 171–172° (Mahrenholtz and Gilbert⁹ record a melting point of 166°).

Anal. Calcd. for $C_{12}H_5O_4Cl_2N_2S_2$: C, 37.89; H, 2.1; N, 7.37; S, 16.84; Cl, 18.68. Found: C, 37.93; H, 2.20; N, 7.55; S, 17.23; Cl, 18.95.

The diethyl ester of 3,3'-azobenzenedisulfonic acid was prepared by refluxing the dichloride in ethanol for 1 hr., precipitating the product with water and recrystallizing from a mixture of methyl acetate and low boiling petroleum ether. The product melted at 107–108° (Mahrenholtz and Gilbert⁹ give 100°).

Anal. Calcd. for $C_{16}H_{18}O_6N_2S_2$: C, 48.24; H, 4.52; N, 7.02; S, 16.08. Found: C, 48.28; H, 4.65; N, 7.02; S, 16.13.

The *S*-benzylthiuronium salt, prepared from the dipotassium salt (above) of 3,3'-azobenzenedisulfonic acid, melted at 217–218°, but was not analyzed. It is presumably the di-*S*-benzylthiuronium salt.

Attempts to prepare 2,2'-azobenzenedisulfonic acid and derivatives. In contrast to the above experience with the *meta* isomer, similar attempts to prepare the *ortho* isomer (2,2'-azobenzenedisulfonic acid) by reduction of the salts

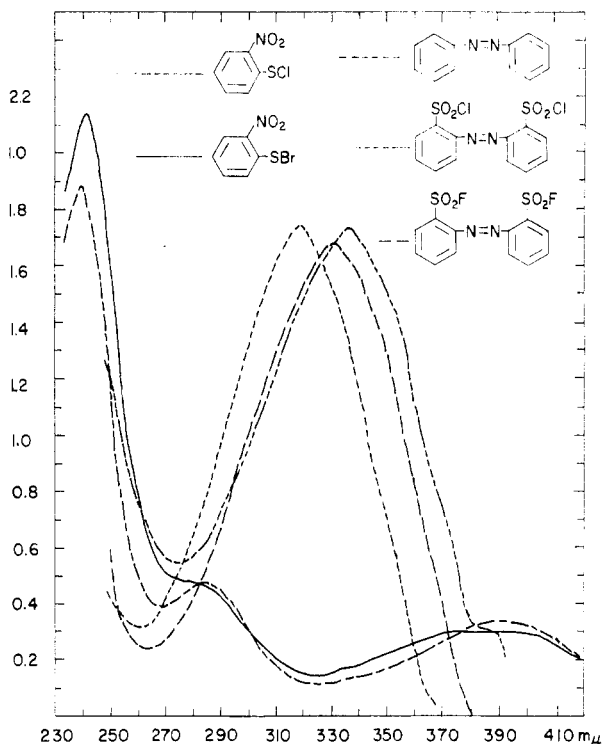


Fig. 1. The ultraviolet spectra of azobenzene, bis(2,2'-chlorosulfonyl)azobenzene and bis(2,2'-fluorosulfonyl)azobenzene, in dioxane, and of 2-nitrobenzenesulfonyl chloride and 2-nitrobenzenesulfonyl bromide, in ethylene chloride

of 2-nitrobenzenesulfonic acid with zinc dust, in alkaline solution, did not yield the desired compound. The attempted conversion of bis(2,2'-methylmercaptoazobenzene) to the sulfonyl chloride, VII [bis-2,2'-chlorosulfonylazobenzene] by chlorination in wet acetic acid, was also not successful.

Bis(2,2'-benzenesulfonyl)azobenzene, XI. III (250 mg.) was dissolved in a mixture of 25 ml. of nitrobenzene and 10 ml. of benzene. One gram of aluminum chloride was added and the reaction mixture heated, under anhydrous conditions, on the hot plate for 2 days. It was then decomposed on ice, the organic layer was separated, dried, diluted with low-boiling petroleum ether, and passed through a column of activated silica. Elution with benzene gave a yellow eluate, from which no solid material could be recovered. Elution with acetone gave a red eluate, which yielded orange crystals. These were recrystallized from acetone, yielding 153 mg. of product, m.p. 250° and giving a 20° m.p. depression on admixture with bis(2,2'-fluorosulfonyl)azobenzene, III, m.p. 256–257°.

Anal. Calcd. for XI, $C_{24}H_{18}O_4N_2S_2$: C, 62.34; H, 3.9; N, 6.20. Found: C, 62.40; H, 4.23; N, 6.06.

A qualitative trace of the ultraviolet absorption spectrum of this product, in dioxane solution, showed that it was very similar to the azo compounds whose spectra are reported in Fig. 1.

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