accounts for 96% of the phenyl groups metered into the furnace. No attempt was made to isolate quantitatively the noncondensable gases since we and others[6] have shown previously that these are mostly hydrogen and methane.

Preparation and disappearance of active species in solution. Toluene (500 g.) was vaporized at atmospheric pressure and the gas was metered at the rate of 0.03 mol./min. to the evacuated pyrolysis system described previously.[3] The gas was pyrolyzed at 1000°, 4 mm. pressure, and 0.004 sec. residence time, and the pyrolyzate was condensed at −78° in 4.5 l. toluene. The disappearance of accumulated titratable species was followed iodometrically at −78°. Two 100-cc. aliquot samples were removed periodically by means of a prechilled pipette. The first was used as a blank. This was warmed to room temperature and then added to 20 cc. of 0.01*N* iodine. The second was added at −78° to the same volume of 0.01*N* iodine. The excess iodine in each flask was back titrated with 0.0192*N* aqueous $Na_2S_2O_3$, and the difference noted was a measure of titratable species. The results are summarized below:

Time (Hr.)	0	1	1.5	2	10	20	30
Concentration mol./l. 10^4	2.6	1.3	0.3	0.2	0.1	0.1	0.08

Identification of benzyl radical and p-xylylene. A second 4-l. solution of pyrolyzate in hexane was prepared as described above via fast flow pyrolysis of 500 g. toluene. The solution contained about 10^{-3} mol. of titratable species when it was quenched at −78° with excess iodine. The resulting solution was warmed to room temperature and the excess iodine was reduced with aqueous sodium thiosulfate. The organic solvent was removed by evaporation and 11 g. dark oil was obtained as residue. This was made to react at 50° with 10 g. NaCN in 200 cc. water methanol solution (1 to 1) over a period of 4 hr. The mixture was separated by extraction with ether. The ether extract was evaporated to dryness leaving a dark oil. This was leached with hot aqueous NaOH for 4 hr. The aqueous solution was acidified and extracted with ether. Infrared analysis indicated that the dark alkali insoluble oil was essentially a mixture of the usual products of fast flow pyrolysis of toluene, namely dibenzyl, and diphenylmethanes. The ether extract was evaporated to dryness leaving 1.1 g. of acidic material as residue. This was separated by vacuum sublimation. The more volatile acid fraction (0.5 g.) was recrystallized from hexane in the form of white needles (m.p. 74.5–76.0°). Its mixed melting point and its infrared spectrum identified the compound as phenylacetic acid. The less volatile fraction (0.3 g.) was recrystallized from hot water in the form of long white needles (m.p. 243–245°). This was identified as *p*-phenylenediacetic acid since its mixed melting point and its infrared spectrum were identical with that of the authentic sample. In another experiment the pyrolyzed toluene stream was condensed at −78° directly into 4 l. hexane saturated with iodine and thereafter the procedure was followed as described above. Again only 1.5 g. acidic material was obtained. Its infrared spectrum indicated that this was a mixture of phenylacetic acid and *p*-phenylenediacetic acid. As a control experiment, 4 l. of 0.2*N* I_2 in toluene solution was treated as described above and no acidic products were isolated. The above results indicate therefore that benzyl radical and *p*-xylylene were present in the original solution in at least the amounts of corresponding acids isolated.

ST. PAUL, MINN.

[CONTRIBUTION OF THE FULMER CHEMICAL LABORATORY, WASHINGTON STATE UNIVERSITY]

Nonbasic Character of Some Aminotrifluoromethyldiphenyl Sulfones

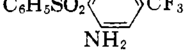
Synthesis of 3-Amino-5-trifluoromethyldiphenyl Sulfone[1]

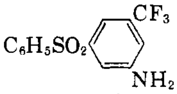
GARDNER W. STACY AND C. RICHARD BRESSON[2]

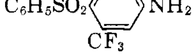
Received May 15, 1959

2-Amino-4-trifluoromethyldiphenyl sulfone (I) and the corresponding bis sulfone IV exhibit extreme nonbasic character by their insolubility in hot 30% hydrochloric acid and lack of reactivity with typical amino group reagents. Such behavior is explained by the strong inductive effect of the sulfone group on an *ortho*-amino group and by enhancement through hydrogen bonding of the resonance interaction involving amino and sulfone groups. Derivative formation in this unreactive series of amino sulfones was accomplished by reaction with acetic anhydride in the presence of a catalytic amount of sulfuric acid to give acetamido compounds. Several studies involving synthesis and structure confirmation of 3-amino-5-trifluoromethyldiphenyl sulfone (II) are described.

It has been found that 2-amino-4-trifluoromethyldiphenyl sulfone (I) exhibits some surprisingly nonbasic properties. It is virtually insoluble in 30% hydrochloric acid and fails to react with acetyl chloride, benzenesulfonyl chloride, or phenyl isothiocyanate to give amino derivatives.[3] Because of these observations, it became of interest to study a group of aminotrifluoromethyldiphenyl sulfones, and especially the isomers of I, 3-amino-5-trifluoromethyldiphenyl sulfone (II) and 4-amino-2-trifluoromethyldiphenyl sulfone (III).


I


II


III

The basicity of these amines was evaluated qualitatively by relative solubility in hot or cold hydrochloric acid of varying concentrations, and the results are summarized in Table I. It is to be

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(1) Presented in part at the 1956 Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 12.

(2) In part abstracted from a thesis submitted by C. Richard Bresson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Washington State University, June 1958.

(3) In part, these experiments were carried out by Richard C. Thamm, Senior in Chemistry, 1952–53.

noted that II and III are far more basic than I, thus indicating a special significance to the *ortho*-orientation of the amino and sulfone groups. This effect was observed again in respect to the bis sulfones IV and V. In the case of the *o*-amino isomer IV, solubility in hot 30% hydrochloric acid is negligible; however, in contrast, the *p*-amino isomer V is completely soluble in cold 10% hydrochloric acid.

TABLE I

SOLUBILITY OF AMINOTRIFLUOROMETHYLDIPHENYL SULFONES IN HYDROCHLORIC ACID

Sulfone	Temp.	HCl Conc., %	Solubility, Wt., Mg.
2-Amino-4-trifluoromethyldiphenyl (I)	H[a]	30	10[b]
3-Amino-5-trifluoromethyldiphenyl (II)	C	10	I
	H	10	60
4-Amino-2-trifluoromethyldiphenyl (III)	C	10	I
	H	10	20
Bis(2-amino-4-trifluoromethylphenyl) (IV)	H	30	I
Bis(4-amino-2-trifluoromethylphenyl) (V)	C	10	S
2,4′-Diamino-4-trifluoromethyldiphenyl (VI)	C	10	I
	H	10	S
4,4′-Diamino-2-trifluoromethyldiphenyl (VII)	C	10	S

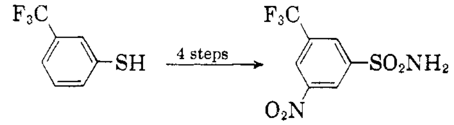
[a] Solubility determinations involved 100 mg. of the sulfone and 10 ml. of hydrochloric acid of the indicated concentration: H, hot—*i.e.*, near boiling; C, cold—*i.e.*, room temperature; I, insoluble; S, soluble. [b] Indicates that 10 mg. dissolved in 10 ml. of hot 30% hydrochloric acid. In each instance the substance was less soluble or insoluble in acid of lesser concentration. In all cases the insoluble material was the amino sulfone rather than the hydrochloride salt.

Fehnel and Carmack[4] have also observed the minimal basicity of an *o*-aminophenyl sulfone, noting that *p*-methylsulfonylaniline is more basic than its *ortho*- isomer. These authors proposed that in the case of *o*-methylsulfonylaniline, the tendency of the aminophenyl chromophore to assume a planar configuration by interaction with the sulfonyl group is augmented by intramolecular hydrogen bonding, thus enhancing the electron deficiency of nitrogen. As an explanation of the nonbasic character of *o*-aminophenyl sulfones, we share the opinion of these authors, but would add that the strong inductive effect of the sulfone group no doubt also plays a part in contributing to the nonbasic character. It also is to be noted that the trifluoromethyl group would exercise an effect in depressing the basicity of the amino group; however, this can be essentially neglected in the present discussion because the trifluoromethyl group occupies the same relative position to the amino group in all isomers.

By reference to sulfones V, VI and VII, it is to be noted that introduction of another amino group in a *para*- position of a second benzene ring mitigates the effect of the sulfone group in decreasing basicity (the electron withdrawing effect of the sulfone group is now distributed over two amino groups). However, as indicated in IV, if both amino groups are in *ortho*- positions, no mitigating effect is observed. Both amino groups here are in position to participate in a system involving resonance and hydrogen bonding. In comparing the isomers II and III, the greater basicity of II would be anticipated since no resonance effect is possible as in the case of the *ortho*- (I) and *para* - (III) orientations.

The difficulties in forming amino derivatives, described above for I, were observed generally for the other amino sulfones studied. It was finally found that acetylation could be accomplished by a procedure employing acetic anhydride and a catalytic amount of sulfuric acid.[5] Information concerning these derivatives is summarized in Table II. It is interesting to note that the *o*-aminodiphenyl sulfones gave the lowest yields. To a degree, these data might be interpreted as a further measure of nonbasic character; however, differences in yields also would most certainly reflect steric factors.

The aminodiphenyl sulfones discussed here have been reported previously[6] with the exception of 3-amino-5-trifluoromethyldiphenyl sulfone (II). Synthetic and structure studies relating to II are now presented in the following account. An initial attempt at synthesis led from *m*-trifluoromethylbenzenethiol (VIII). The thiol group was converted to a sulfonic acid group, a nitro group was introduced, and subsequently a sulfonyl chloride group was formed. Although the sulfonyl chloride was not readily purified, it was characterized by the corresponding sulfonamide IX. This attempted synthesis of II failed, however, because the sulfonyl chloride did not react successfully with benzene in a Friedel-Crafts procedure to form a sulfone.



VIII IX

The desired amino sulfone II finally was obtained by a synthesis starting with 3-amino-5-nitrobenzo-

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(4) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **72**, 1292 (1950).

(5) A. I. Vogel, *A Text-Book of Practical Organic Chemistry*, 2nd. ed., Longmans, Green and Co., New York, 1951, p. 556.

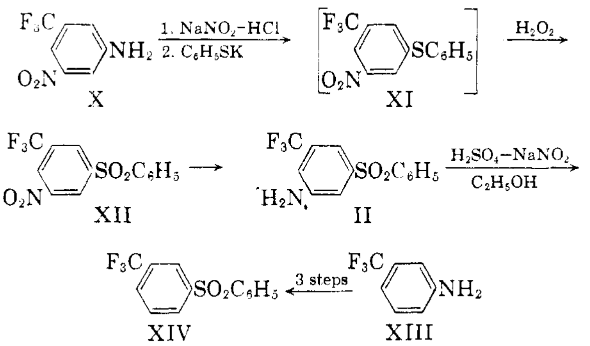
(6) G. W. Stacy, C. R. Bresson, R. E. Harmon, and R. C. Thamm, *J. Org. Chem.*, **22**, 298 (1957).

TABLE II

ACETYL DERIVATIVES OF AMINOTRIFLUOROMETHYLDIPHENYL SULFONES

Corresp. Sulfone	Yield, %[a]	Appearance[b]	M.P.[c]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
I	49	Long needles	147.5–148	$C_{15}H_{12}F_3NO_3S$	52.47	52.36	3.52	3.65	9.34	9.18
II	64	Needles	160–160.5	$C_{15}H_{12}F_3NO_3S$	52.47	52.30	3.52	3.47	9.34	9.20
III	81[d]	Plates	177–178	$C_{15}H_{12}F_3NO_3S$	52.47	52.48	3.52	3.55	9.34	9.56
IV	33	Fine plates	242–243	$C_{18}H_{14}F_6N_2O_4S$	46.16	46.18	3.01	3.21	6.85	6.68
V	65	Fine needles	263–264	$C_{18}H_{14}F_6N_2O_4S$	46.16	46.12	3.01	3.24	6.85	7.05
VI	8[e]	Plates	215–216	$C_{17}H_{15}F_3N_2O_4S$	51.00	51.20	3.78	3.81	8.01	7.79
VII	50	Fine plates	262–262.5	$C_{17}H_{15}F_3N_2O_4S$	51.00	51.01	3.78	3.96	8.01	8.07

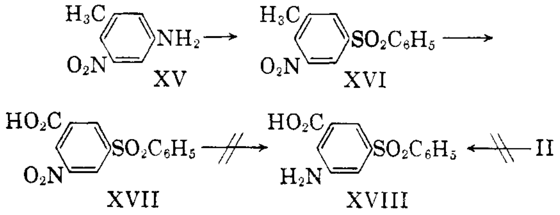
[a] Yields reported are those of the recrystallized products. [b] Analytical samples were recrystallized several times in each instance from 60% ethanol unless otherwise stated; colorless crystals were obtained in all cases. [c] M.p. of analytical sample. [d] Recrystallized from 95% ethanol. [e] This substance was obtained in a quantitative crude yield, but substantial losses were sustained in recrystallizing the material from 95% ethanol.



trifluoride (X). By way of the Ziegler procedure,[7] the amine X reacted to give a mixture from which the anticipated sulfide XI could not be isolated. Other workers[7,8] have reported similar difficulties in isolating sulfides formed by this method. Isolation of XI was, therefore, bypassed, and the crude reaction mixture was treated with hydrogen peroxide to oxidize any sulfide present to the corresponding sulfone XII. Although the product could be isolated by tedious fractional crystallization, chromatography produced the desired XII more conveniently in a 21% over-all yield. The final step, involving a stannous chloride–hydrochloric acid reduction, afforded II in a 77% yield.

The *meta*- orientation of the sulfone and trifluoromethyl groups and hence indirectly the *meta*- orientation of these two groups to the amino group in II was established in the following manner. The sulfone II was deaminated to *m*-trifluoromethyldiphenyl sulfone (XIV), which in turn was prepared in an unequivocal manner from the known amine XIII. The preparation again involved the Ziegler method for introducing a sulfide group at the site of an amino function, and again the sulfide was not isolated but oxidized to the sulfone XIV, which was shown by a mixed melting point determination and infrared spectrum to be identical with the sample of XIV formed by the deamination of II.

A further structure study of II was pursued unsuccessfully, but because several new intermediates and observations of interest were made in the course of this work, it is presented. As it is known that the trifluoromethyl group can frequently be converted to a carboxyl group,[9] interrelationship of a sample obtained from II with that formed by synthesis from XV was undertaken. In turn, the preparation of known 3,5-dinitrotoluene in route to the prerequisite XV encountered findings that deserve brief comment. In our hands, procedures involving hypophosphorous acid[10] proved unsatisfactory in the deamination of 3,5-dinitro-*p*-toluidine. A method by Cohen and McCandlish,[11] which had been presented incompletely, has been reinvestigated, and a definitive procedure giving yields of 92% was developed. The fact that this procedure employs ethanol is of interest, as ordinarily hypophosphorous acid is the reagent of choice in deaminations. 3-Amino-5-nitrotoluene (XV) was converted to the new sulfone XVI by the Ziegler sulfide preparation, followed by hydrogen peroxide oxidation. The methyl group of XVI was oxidized by the action of sodium dichromate–sulfuric acid to give a 41% yield of 3-carboxy-5-nitrodiphenyl sulfone (XVII).



Although it was found that isomeric 2-amino-4-trifluoromethyldiphenyl sulfone (I) on treatment with fuming sulfuric acid gave 2-amino-4-carboxydiphenyl sulfone (XIX) in 60% yield, it was not

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(7) (a) J. H. Ziegler, *Ber.*, **23**, 2469 (1890); (b) C. Graeber and C. Schultess, *Ann.*, **263**, 1 (1891); W. S. Weeden and H. W. Doughty, *Am. Chem. J.*, **33**, 386 (1903); (c) G. E. Hilbert and T. B. Johnson, *J. Am. Chem. Soc.*, **51**, 1526 (1929).

(8) D. A. Shirley and E. A. Lehto, *J. Am. Chem. Soc.*, **79**, 3481 (1957).

(9) G. M. Le Fave, *J. Am. Chem. Soc.*, **71**, 4148 (1949).

(10) N. Kornblum, *Org. Reactions*, Vol. **II**, 296 (1944).

(11) J. B. Cohen and D. McCandlish, *J. Chem. Soc.*, **87**, 1271 (1905).

possible to carry out a parallel formation of XVIII from II. Concurrent difficulties in this connection and in carrying out the reduction of XVII led us to discontinue this phase of the work.

EXPERIMENTAL[12]

Acetamido derivatives. A mixture of 500 mg. of the aminotrifluoromethyldiphenyl sulfone, 3–4 ml. of acetic anhydride, and two drops of concentrated sulfuric acid was allowed to stand 1–3 days. Yields of only about 10% were obtained with the *o*-amino compounds after 1 day, so that a 3-day period was employed in these cases. The reaction mixture finally was poured into 50 ml. of cold water, and the product was recrystallized from 60 or 95% ethanol. Results for the individual products are summarized in Table II.

m-Trifluoromethylbenzenethiol (VIII).[13] To a stirred mixture of 30 ml. of concentrated hydrochloric acid and 50 g. of ice was added 16.1 g. (0.10 mol.) of *m*-aminobenzotrifluoride,[14] the amine hydrochloride separating. While the temperature was maintained below 5° by cooling in an ice bath, a solution of 7.60 g. (0.11 mol.) of sodium nitrite in 16 ml. of water was added dropwise with stirring. This diazonium salt solution was added with stirring while the temperature was maintained at 40° to a solution of 22.0 g. (0.37 mol.) of potassium hydroxide and 20.0 g. (0.12 mol.) of potassium ethyl xanthate. After the mixture had been stirred for an additional 0.5 hr., cooled, and extracted with ether, the ether was removed, and the residual oil was taken up in 100 ml. of 95% ethanol. While this solution was being heated under reflux, 30.0 g. of potassium hydroxide was added slowly. After the mixture had been heated an additional 5 hr., cooled, and made strongly acidic with 6*N* sulfuric acid, it was steam distilled in the presence of zinc powder. The distillate was extracted with ether, and the ether solution was dried over anhydrous magnesium sulfate. The solvent was removed, and the product was distilled under reduced pressure to give a foul smelling liquid; yield, 9.58 g. (54%), b.p. 55–59° (13–14 mm.), n_D^{25} 1.4882, lit.[15] b.p. 84–86° (40 mm.).

Anal. Calcd. for $C_7H_5F_3S$: C, 47.19; H, 2.83; S, 17.94. Found: C, 47.36; H, 3.06; S, 18.04.

3-Trifluoromethyl-5-nitrobenzenesulfonamide (IX). Treatment of 3.44 g. (0.02 mol.) of the thiol VIII with 20 ml. of 30% hydrogen peroxide in 5 ml. of acetic acid converted it (after refluxing for 5 hr.) to the corresponding sulfonic acid; this was isolated as the sodium salt in a yield of 4.30 g. (87%). To this was added 19 ml. of fuming nitric acid and 17 ml. of 30% fuming sulfuric acid, resulting (after being heated at 90° for 6 hr. and neutralization of the reaction mixture) in the formation of 3.50 g. (68%) of crude sodium 3-nitro-5-trifluoromethylbenzenesulfonate. A mixture of 6.0 g. (0.02 mol.) of this crude sodium salt, 3.20 g. (0.016 mol.) of phosphorus pentachloride, and 20 ml. of phosphorus oxychloride was heated at 140°. This gave 3.40 g. (58%) of a crude sulfonyl chloride, which could not be purified or converted to the corresponding sulfone in a Friedel Crafts reaction with benzene.

However, it was possible to convert the crude sulfonyl chloride to the corresponding sulfonamide IX by adding 500 mg. of the crude oil to 20 ml. of concentrated ammonium hydroxide. The solution was allowed to evaporate to dryness at room temperature to yield 600 mg. of a light yellow solid. This was recrystallized from 95% ethanol, resulting in 100 mg. (22% yield) of 3-trifluoromethyl-5-nitrobenzenesulfonamide (IX), m.p. 140.5–141°.

Anal. Calcd. for $C_7H_5F_3O_4N_2S$: C, 31.11; H, 1.87; S, 11.87. Found: C, 31.20; H, 1.79; S, 11.63.

3-Amino-5-nitrobenzotrifluoride (X). This procedure is adapted from one reported by Finger and Reed[16]; their original procedure employed a two-fold excess of *ethanolic* ammonium sulfide. We obtained a somewhat better result using *methanol* as solvent and a three-fold excess. A solution of 11.8 g. (0.05 mol.) of 3,5-dinitrobenzotrifluoride[17] in methanolic ammonium sulfide [prepared from 36.0 g. (0.15 mol.) of sodium sulfide nonahydrate, 32.0 g. (0.60 mol.) of ammonium chloride, and 150 ml. of methanol] was heated under reflux for 5 hr. The reaction mixture was concentrated by evaporation, cooled, and filtered. The residue was purified by dissolving the amine in hot 20% hydrochloric acid. The resulting solution was cooled, and the 3-amino-5-nitro benzotrifluoride (X) was precipitated by the addition of 20% sodium hydroxide solution; yield 7.62 g. (74%), m.p. 78–79°, lit.[16] m.p. 80–81.5°.

3-Trifluoromethyl-5-nitrodiphenyl sulfone (XII). To 3.05 g. (0.015 mol.) of X was added 30 ml. (0.36 mole) of concentrated hydrochloric acid, the mixture being heated to effect solution. This was filtered and cooled in an ice bath, and a cold solution of 1.04 g. (0.015 mole) of sodium nitrite (dissolved in 5 ml. of water) was added dropwise. After 0.5 hr. the diazonium salt solution was added to a cold, stirred mixture of 3.30 g. (0.03 mol.) of thiophenol, 39.0 g. (0.70 mol.) of potassium hydroxide, 50 ml. of water, and 2.0 g. of copper powder. Stirring was continued for 2 hr. at an ice bath temperature and then for 2 hr. at 60°. The mixture was extracted with ether (3 × 30 ml.), and the ether then was removed by evaporation leaving a reddish black oil. This residue was dissolved in 50 ml. of glacial acetic acid, the solution was heated to 90°, and 40 ml. of 30% hydrogen peroxide was added over a period of 4 hr. The reaction mixture was heated under reflux overnight, cooled, and poured into water; it was then neutralized with 10% sodium hydroxide solution and extracted with ether. The ether was removed by evaporation, and the residue was chromatographed on alumina. The sulfone XII was isolated from the benzene ether eluents and was recrystallized from 85% ethanol to give 1.07 g. (21% yield), m.p. 128–129°.

Anal. Calcd. for $C_{13}H_8F_3NO_4S$: C, 47.13; H, 2.43; S, 9.68. Found: C, 46.98; H, 2.49; S, 9.48.

3-Amino-5-trifluoromethyldiphenyl sulfone (II). From 500 mg. (1.50 mmol.) of XII, which was reduced with stannous chloride–hydrochloric acid solution,[6] 460 mg. of crude II was obtained; this was recrystallized from 60% ethanol and yielded 350 mg. (77%), m.p. 161–162°.

Anal. Calcd. for $C_{13}H_{10}F_3NO_2S$: C, 51.82; H, 3.35; S, 10.64. Found: C, 51.82; H, 3.35; S, 10.49.

m-Trifluoromethyldiphenylsulfone (XIV). To 20 ml. of 10% hydrochloric acid was added 4.04 g. (0.025 mole) of *m*-aminobenzotrifluoride (XIII).[14] The mixture was cooled to 0° in an ice bath, and a solution of 1.73 g. (0.025 mol.) of sodium nitrite in 10 ml. of water was added dropwise. After standing for 0.5 hr. at 0°, the clear diazonium solution was added dropwise to a stirred, cooled (ice bath temperature) mixture of 5.60 g. (0.10 mol.) of potassium hydroxide, 5.50 g. (0.05 mol.) of thiophenol, and 2 g. of copper powder in 50 ml. of water. The mixture was stirred for 1 hr. at 0° and then at 70° for 2 hr. After the reaction mixture had cooled to room temperature, a red oil was extracted with ether (3 × 25 ml.). The solvent was evaporated from the ether extracts,

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(12) All melting points are corrected. The microanalytical work was performed by Galbraith Laboratories, Knoxville, Tenn., and by Weiler and Strauss Laboratories, Oxford, England.

(13) Adapted to this preparation from a procedure reported by D. S. Tarbell and D. K. Fukushima, *Org. Syntheses*, Coll. Vol. III, 809 (1955).

(14) Obtained from Halogen Chemicals Inc., 616 King Street, Columbia 5, S. C.

(15) Prepared previously by a Grignard method by Soper, C. W. Whitehead, O. K. Behrens, J. C. Corse, and R. G. Jones. *J. Am. Chem. Soc.*, 70, 2849 (1948).

(16) G. C. Finger and F. H. Reed, *J. Am. Chem. Soc.*, 66, 1972 (1944).

(17) Prepared by the method of Finger and Reed in a 55% yield (ref. 16).

and the residual dark oil was dissolved in 50 ml. of a 1:5 solution of acetic anhydride–glacial acetic acid. The mixture was heated to 90°, and 30 ml. of 30% hydrogen peroxide was added over a 4-hr. period. The mixture was heated under reflux, an additional 10 ml. of 30% hydrogen peroxide was added, and the mixture was heated for 1 hr. The solution was poured into 1 l. of ice water, and the mixture was made basic with 20% sodium hydroxide solution. The yield of red-brown semisolid, obtained after filtering and drying, was 5.23 g. (73%). This was purified by chromatography using alumina and the customary sequence of solvents, followed by recrystallization from 95% ethanol to give 3.53 g. (49%), m.p. 77–78°.

Anal. Calcd. for $C_{13}H_9F_3SO_2$: C, 54.54; H, 3.17. Found: C, 54.33; H, 3.16.

Conversion of 3-amino-5-trifluoromethyldiphenyl sulfone (II) *to m-trifluoromethyldiphenyl sulfone* (XIV). A mixture of 300 mg. (0.99 mmol.) of II, 6 ml. of absolute ethanol, and 1.5 ml. of concentrated sulfuric acid was heated to the reflux temperature. Then 0.90 g. of sodium nitrite was added in small portions over a period of 1 hr., and the mixture was heated for an additional 1-hr. period. When the mixture was poured onto 100 g. of ice, a red oil separated. After the supernatant liquid had been decanted, the oil was taken up in benzene, and the solution was dried over anhydrous sodium sulfate. Chromatography followed by recrystallization from ethanol gave a yield of 150 mg. (53%), m.p. 77–78°. Admixture of this sample with the material formed from *m*-aminobenzotrifluoride (XIII) resulted in no depression in melting point (mixed m.p. 77–78°), and the infrared absorption spectra[18] of the two samples were identical.

3,5-Dinitrotoluene. To 21.2 g. (0.11 mol.) of 3,5-dinitro-*p*-toluidine[19] in 400 ml. of absolute ethanol was added 100 ml. of concentrated sulfuric acid with swirling and cooling. After the resulting mixture had been heated to the reflux temperature, 63.6 g. (0.92 mol.) of sodium nitrite was added through the condenser in small portions during a period of 2.5 hr. It was necessary to wash down the condenser frequently with absolute ethanol to prevent the sodium nitrite from accumulating on the condenser walls. After effervescence had ceased, the mixture was diluted with water and poured into a 1-l. mixture of ice water. The mixture was filtered, and the residue was washed and dried; yield of deaminated product, 18.0 g. (92%), m.p. 89–90°, lit.[11] m.p. 93°. A small portion was recrystallized from aqueous ethanol, m.p. 92–93°; however, the crude product was satisfactory for the present work.

3-Methyl-5-nitrodiphenyl sulfone (XVI). The details of this procedure are similar to those described for XII and XIV. A solution of 1.90 g. (0.013 mol.) of 3-amino-5-nitrotoluene[20] in 38 ml. of concentrated hydrochloric acid and 10 ml. of water was diazotized by the dropwise addition of 89.7 mg. (0.013 mol.) of sodium nitrite in 7 ml. of water. The resulting solution was added to a mixture of 2.84 g. (0.026 mol.) of thiophenol, 40.0 g. (0.71 mol.) of potassium hydroxide, and 1.5 g. of copper powder in 50 ml. of water. The reaction mixture was extracted with ether, and after the solvent had been removed by evaporation, the residual oil was taken up in 40 ml. of glacial acetic acid. The resulting solution was heated to 90°, and 25 ml. of 30% hydrogen peroxide was added. After the reaction was complete, the mixture was poured into ice water and was neutralized with 20% sodium hydroxide solution. The mixture was extracted with ether, the solvent was distilled from the combined extracts, and the residue was chromatographed over alumina using the customary sequence of solvents. The sulfone was isolated from the benzene ether fractions, and after recrystallization from 85% ethanol, the yield was 560 mg. (16%), m.p. 133.5–134.5°.

Anal. Calcd. for $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; S, 11.56. Found: C, 56.30; H, 4.04; S, 11.54.

3-Carboxy-5-nitrodiphenyl sulfone (XVII). In an adaptation of a procedure reported by Kamm and Mathews,[21] 1.44 g. of concentrated sulfuric acid in 0.1 ml. portions was added over a period of 15 min. to a stirred mixture of 200 mg. (0.72 mmol.) of XVI and 290 mg. (0.97 mmol.) of sodium dichromate dihydrate in 1.2 ml. of water. The mixture was heated at 120° for 0.5 hr., cooled, and diluted with 20 ml. of water. The green residue obtained after filtering the mixture was treated with 20 ml. of 20% sodium hydroxide solution; the resulting mixture was filtered, and the filtrate was acidified with dilute sulfuric acid. The crude product obtained amounted to 110 mg. (55% yield), m.p. 163–164°. The sodium hydroxide–insoluble residue from above was starting material; 70 mg. (40% recovery), m.p. 130–131° (mixed m.p. 133–134°). Recrystallization of crude XVII from aqueous acetic acid resulted in 90 mg. (45% yield), m.p. 167.5–168.5°.

Anal. Calcd. for $C_{13}H_9NO_6S$: C, 50.81; H, 2.95; S, 10.43. Found: C, 51.06; H, 2.86; S, 10.31.

2-Amino-4-carboxydiphenyl sulfone (XIX). To 200 mg. (0.66 mmol.) of 2-amino-4-trifluoromethyldiphenyl sulfone (I) was added 1.0 ml. of concentrated sulfuric acid, and the solution was heated at 200° for 15 min. Then 0.4 ml. of 15% fuming sulfuric acid was added, and heating was continued for 0.5 hr. The solution was cooled and poured onto 20 g. of ice; the resulting solution was made basic and extracted with ether (3 × 10 ml.) to remove colored impurities. The aqueous phase was made acidic with dilute sulfuric acid, and the precipitate was removed by filtration; yield, 120 mg. (66%), m.p. 283° (dec.). Recrystallization from 85% ethanol afforded colorless needles, 110 mg. (60% yield), m.p. 286–287° (dec.).

Anal. Calcd. for $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; S, 11.56. Found: C, 56.10; H, 3.88; S, 11.78.

Acknowledgment. This investigation was supported in part by research funds of Washington State University, Project 234. We are indebted to Mr. David L. Frasco of the Division of Industrial Research of Washington State University for determination of infrared absorption spectra.

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(18) The infrared absorption spectra were determined by means of a Perkin-Elmer double beam infrared spectrometer, model 21. The samples were prepared by sublimation onto a sodium chloride plate.

(19) This substance and other prior intermediates were prepared by methods reported by R. A. Morton and A. McGookin, *J. Chem. Soc.*, 901 (1934).

(20) Prepared in 79% yield by an alcoholic ammonium sulfide reduction of 3,5-dinitrotoluene (*cf.* ref. 19).

(21) O. Kamm and A. O. Mathews, *Org. Syntheses*, **Coll. Vol. I**, 392 (1956).