

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

Aromatic Sulfonic Acid Anhydrides

BY LAMAR FIELD

The anhydrides of benzene- and *p*-toluenesulfonic acid were prepared in yields of about 50% by a novel method using phosphorus pentoxide, which appears to be superior in certain respects to methods previously described. The anhydride gives results superior to those obtained using the corresponding sulfonyl chloride in the Friedel-Crafts sulfone synthesis, the sulfonylation of diethyl malonate and the synthesis of a thioisulfonate. The mode of reaction of benzenesulfonic anhydride with hydrogen bromide, certain Grignard reagents, pyridine and sodium sulfite was established.

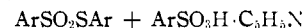
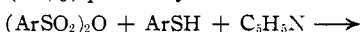
Although anhydrides of sulfonic acids have been known for many years, very little attention has been given to their synthesis or reactions. Benzenesulfonic anhydride may be prepared from silver benzenesulfonate and benzenesulfonyl chloride,¹ although this method is rather expensive and inconvenient. Several anhydrides have been prepared by the reaction of thionyl chloride with sulfonic acids or their salts²; the sulfonyl chloride may also be obtained, however, and the relative amounts of the two products appear to depend upon trace impurities in the thionyl chloride. A recent report³ describes the conversion of benzenesulfonyl chloride to the anhydride by oxalic acid. Other reactions in which sulfonic anhydrides are formed seem to be of limited utility as general preparative methods.

This paper reports the conversion of benzene- and *p*-toluenesulfonic acid, intended to serve as model substances, to the corresponding anhydrides in about 50% yields by heating with excess phosphorus pentoxide mixed with an inert support to facilitate subsequent extraction.

The melting point ranges of the anhydrides were rather broad. It was considered important to determine whether this indicated considerable impurity or merely resulted from an unusually great influence of impurities on the melting point.^{2a} The breadth of the melting range of *p*-toluenesulfonic anhydride appears to be a consequence of the relatively high freezing point depression constant (approximately 10) and the very low m.p. (38°)⁴ of the sulfonic acid, the most likely impurity; it is probably also influenced by ionization of the sulfonic acid. The freezing point of a typical sample of *p*-toluenesulfonic anhydride, which in a capillary softened at 85° and melted at 115–127.5°, was consistent with the presence of only 2% of completely ionized *p*-toluenesulfonic acid. Several reactions of aromatic sulfonic anhydrides are reported for the first time in this paper. In some of these, the results obtained were superior to those given by sulfonyl chlorides in similar reactions.

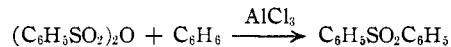
p-Tolyl *p*-toluenethioisulfonate has been obtained in 25% yield from the reaction of the sulfonyl chloride and the thiol.⁵ Reaction of *p*-toluenesulfonic anhydride and *p*-thiocresol in the presence of pyridine in this Laboratory gave very pure *p*-tolyl *p*-toluenethioisulfonate in 71% yield, together with 16% of di-*p*-tolyl disulfide. Phenyl benzenethioisulfonate was obtained in lower yield

(38%) probably because it is a less stable substance.



Evidence was obtained that the pyridine-catalyzed reactions of sulfonic anhydrides probably proceed through the formation and subsequent reaction of an adduct analogous to those which pyridine forms with benzenesulfonyl chloride.⁶ Thus removal of the solvent from a solution of pyridine and benzenesulfonic anhydride left a solid having an m.p. higher than that of the anhydride. The solid was readily soluble in water (unlike the anhydride), and had a hydrolysis equivalent in reasonable agreement with that expected for a 1:1 combination of the anhydride and pyridine. The complex, probably 1-benzenesulfonylpyridinium benzenesulfonate, reacted readily with phenol giving phenyl benzenesulfonate in 87% yield.

The Friedel-Crafts reaction of benzenesulfonyl chloride with benzene and one molar proportion of aluminum chloride reportedly gives diphenyl sulfone in 82% yield.⁷ In this Laboratory use of more recent techniques gave an apparently purer product by this method in 70% yield. On the other hand, diphenyl sulfone was obtained in 99% yield by using benzenesulfonic anhydride with two molar proportions of aluminum chloride under similar conditions.



A previous preparation of sulfones by reaction of aromatic sulfonic acids, aromatic hydrocarbons and phosphorus pentoxide⁸ undoubtedly involved aromatic sulfonic anhydrides as intermediates, although this possibility was apparently not considered.

Beckurts and Otto⁷ reported that no reaction occurred in the presence of aluminum chloride between benzenesulfonyl chloride and bromobenzene, both compounds being recovered unchanged, although chlorobenzene gave the corresponding sulfone in 87% yield. Use of benzenesulfonic anhydride in the present study resulted, however, in the formation of phenyl *p*-bromophenyl sulfone in 74% yield.

The reaction of benzenesulfonyl chloride with diethyl sodiomalonate leads principally to products resulting from reduction of the sulfonyl chloride by the enolate,⁹ although diethyl phenylsulfonylmalonate was also formed in unstated yield, possibly by

(1) O. C. Billeter, *Ber.*, **38**, 2015 (1905).

(2) (a) H. Meyer and K. Schlegel, *Monatsh.*, **34**, 561 (1913); (b) H. Meyer, *ibid.*, **36**, 719 (1913); (c) H. Meyer, *Ann.*, **433**, 327 (1923).

(3) R. C. Shepherd, *J. Org. Chem.*, **12**, 275 (1947).

(4) K. H. Slotta and W. Franke, *Ber.*, **63**, 684 (1930).

(5) D. T. Gibson, C. J. Miller and S. Smiles, *J. Chem. Soc.*, **127**, 1821 (1925).

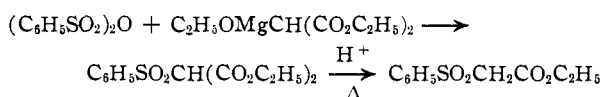
(6) G. L. Schwartz and W. M. Dehu, *This Journal*, **39**, 2451 (1917).

(7) H. Beckurts and R. Otto, *Ber.*, **11**, 2066 (1878).

(8) A. Michael and A. Adair, *ibid.*, **10**, 583 (1877); **11**, 116 (1878).

(9) C. L. Jackson and F. C. Whitmore, *This Journal*, **37**, 1915 (1915).

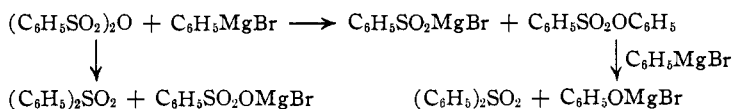
reaction of the sodium benzenesulfinate and diethyl chloromalonate formed in the reduction step. The reaction of benzenesulfonyl anhydride with diethyl ethoxymagnesiummalonate has now been found to result in diethyl phenylsulfonylmalonate in 53% yield. Characterization was effected by the neutral equivalent of the ester, and also by hydrolysis and decarboxylation which gave ethyl phenylsulfonylacetate identical with an authentic sample.



Reaction of benzenesulfonyl anhydride with diethyl sodiomalonate gave diethyl phenylsulfonylmalonate in 24% yield.

A reduction reaction similar to that referred to above also predominates in the reaction of sulfonyl halides with sodium phenylacetylide,¹⁰ and a sulfone is not obtained. An attempt in this Laboratory to prepare phenyl phenylethynyl sulfone by reaction of sodium phenylacetylide and benzenesulfonyl anhydride was also unsuccessful and gave only an intractable oil, although a reaction apparently occurred at 5°.

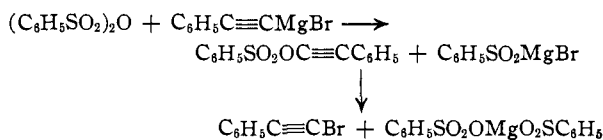
The reaction of aromatic sulfonyl halides with Grignard reagents¹¹ is complex, giving usually a mixture of products. The reaction of benzenesulfonyl anhydride with phenylmagnesium bromide at -30 to -20° likewise resulted in a mixture of products, including a benzenesulfonic acid salt (isolated as benzenesulfonamide in 8% yield), a benzenesulfonic acid salt (35%), phenol (2%) and diphenylsulfone (20%). The course of the reaction may be represented, at least in part, by the equations



Addition of the anhydride to the phenylmagnesium bromide solution without cooling resulted in a mildly exothermic reaction, but the only isolable product was a trace of diphenyl sulfone. Similarly, no appreciable amount of solid could be isolated after the addition of methylmagnesium iodide to the anhydride even at -30 to -20°.

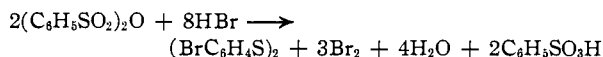
Phenylethynylmagnesium bromide, like sodium phenylacetylide, forms phenylethynyl chloride upon reaction with an aromatic sulfonyl chloride,¹² rather than a phenylethynyl aryl sulfone. The reaction of phenylethynylmagnesium bromide and benzenesulfonyl anhydride likewise did not lead to sulfone formation, but unexpectedly resulted in phenylethynyl bromide (84% yield), characterized by physical and chemical properties and by hydration to ω -bromoacetophenone. The formation of this bromide is seemingly best explained by assuming that phenylethynyl benzenesulfonate formed as an intermediate, alkylates a magnesium bromide salt present in the reaction mixture. Since evidence was obtained for the formation of a salt of

benzenesulfinic acid in the reaction the course of the reaction is probably best represented by the equations



The reduction of sulfonyl chlorides using sodium sulfite affords a method useful for preparing aromatic sulfinic acids. Using similar conditions,¹³ we have reduced benzenesulfonyl anhydride to benzenesulfinic acid in 62% yield, although the product was less pure and more difficult to purify than those usually obtained from benzenesulfonyl chloride.

Proell¹⁴ has described the conversion of alkanesulfonyl anhydrides to the corresponding sulfonyl chlorides by reaction with hydrogen chloride. An attempt was made to extend this reaction to the preparation of benzenesulfonyl bromide which is rather difficultly obtainable. When hydrogen bromide was passed through molten benzenesulfonyl anhydride, however, the product formed was bis-(*p*-bromophenyl) disulfide (57% yield). Characterization was effected by analysis, by identity with authentic material in physical and chemical properties, and by reduction to *p*-bromothiophenol. The result obtained is apparently consistent with the over-all equation



The para position of the bromine atoms suggests that benzenesulfonyl bromide was formed, but was reduced to diphenyl disulfide which was then brominated by bromine formed as an oxidation product. The formation of disulfides in reactions expected to produce sulfonyl bromides has also been observed by Kohlhasse.¹⁵

Preliminary results indicate that several of the reactions described above occur also with alkanesulfonyl anhydrides. Studies in this direction are being continued.

Acknowledgment.—The author is indebted both to the Research Corporation and to the Carnegie Foundation and Vanderbilt University jointly for generous grants during the course of this work.

Experimental¹⁶

Preparation of Anhydrides (a) Benzenesulfonyl Anhydride.—One-half of a mixture of 307 g. of phosphorus pentoxide, 38 g. of Super-cel kieselguhr and 38 g. of Gooch asbestos was mixed with 150 g. of benzenesulfonyl acid (sesquihydrate). The hot mixture was allowed to stand for one-half hour and was then heated in an oil-bath at 100° while the remainder of the mixture was mixed in as well as possible during two hours. After heating at 100° with occasional mixing for five hours, 350 ml. of pure ethylene chloride was added, and the mixture was heated under

(10) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 506, 514.

(11) Ref. 10, p. 506.

(12) R. Truchet, *Ann. chim.*, **16**, 327 (1931).

(13) The present procedure was based on one described for a sulfonyl chloride by S. Smiles and C. M. Bere, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 7.

(14) W. A. Proell, U. S. Patent 2,489,317 (1949) [C. A., **44**, 1527 (1950)].

(15) A. H. Kohlhasse, *This Journal*, **54**, 2441 (1932).

(16) Melting points are corrected and boiling points are uncorrected. Concentrations were effected under reduced pressure. Analyses are by Clark Microanalytical Laboratory, Urbana, Ill.

reflux for 10 minutes with occasional shaking. The stoppered flask was then shaken well and the liquid decanted through a plug of glass wool in the neck. After the process had been repeated five times with 100-ml. portions of solvent, the combined extracts were concentrated and gave 84.8 g. (70%) of light tan solid, m.p. 60–85° (softening about 55°).¹⁷

The product was recrystallized by passing a dry ether-benzene¹⁸ (10:1) solution through a filter stick (sintered glass) under pressure of dry nitrogen and removing the solvent with the filter stick after crystallization, and was then dried at 1 mm. pressure. There was obtained 60.3 g. (50%) of nearly colorless granular crystals, m.p. 81–89° (softening about 80°). A second crop of 12.3 g. (10%), m.p. 60–81° (softening about 58°) was obtained from the mother liquor. Further recrystallization from ether gave nearly colorless long thin tablets, m.p. 88–91° (softening about 75°); hydrolysis equiv., 150 (calcd. 149).

The product was converted to benzenesulfonamide in 75% yield, m.p. and mixture m.p. 154.5–155.5°.

Authentic benzenesulfonic anhydride was prepared¹ in 90% yield by heating silver benzenesulfonate and benzenesulfonyl chloride for 3.5 hours, but the product was very oily. Recrystallization from ether gave material of m.p. 61–84° in 47% yield; further recrystallization gave a product having a constant m.p. of 88.5–91.5° (softening about 79°) which did not depress the m.p. of the pure material prepared using phosphorus pentoxide.

Both samples when allowed to stand in air caked slightly in one hour and almost completely liquefied in 2.5 hours. A sample of anhydride dropped in m.p. from 85–91° to 62–87° upon standing with occasional brief exposure in an evacuated flask for two months. The anhydride is less sensitive to attack when suspended in water than when exposed to air,²³ but attempted purification by washing an ethylene chloride solution with ice-water and then drying over phosphorus pentoxide resulted in a decrease in m.p. from 80–90° to 62–75°, although 94% was recovered.

Use of 382 g. of phosphorus pentoxide, 38 g. of Super-cel and 12.7 g. of asbestos with 248 g. of the acid resulted in a 52% yield (after recrystallization), m.p. 79.5–90.5° (softening about 60°). Appreciable further reduction of the amount of phosphorus pentoxide or of the time or temperature of heating seemed to give less satisfactory results. An attempt to use a 75% excess of phosphorus pentoxide with ethylene chloride heated under reflux as a reaction medium gave very poor results.

(b) *p*-Toluenesulfonic Anhydride.—This anhydride was prepared by using 214 g. of phosphorus pentoxide, 14 g. of Super-cel, 7 g. of asbestos and 190.2 g. of *p*-toluenesulfonic acid (monohydrate) in essentially the above procedure, except that the temperature was 125° and the time of final heating was 6.5 hours. The solid obtained (143.7 g., 88%; m.p. 65–115°) after recrystallization from ether-benzene (1:1) gave 86.9 g. (53%) of light-brown prisms, m.p. 115–130° (softening about 75°), which after standing for six weeks under vacuum with occasional exposure had a capillary m.p. of 115–127.5° (softening about 85°) and a freezing point (cooling curve) of 125.90°. A second recrystallization gave 45% of light-gray prismatic rods, m.p. 127.5–131°.

Further recrystallization resulted in colorless lath-like prisms with a constant m.p. of 129.5–131.5° (softening about 120°); m.p. reported,²⁰ 125°. The freezing point, determined by the cooling-curve method with precautions for exclusion of moisture, was 128.53°. The molal freezing point depression constant was 10.2; a sample (0.0900 g.) of 2,4-dinitrotoluene with 4.840 g. of anhydride resulted in a ΔT of 1.07° (K_f , 10.5), and a sample (0.0992 g.) of methyl phenyl sulfone with 5.499 g. of anhydride in a ΔT of 1.13° (K_f , 9.8).

Heating for 45 minutes in boiling water was required to effect solution of a small sample; hydrolysis equiv., 166 (calcd., 163).

(17) M.p. tubes were loaded with the anhydrides in a dry-box, or by insertion into a portion of material ground against the flask bottom. The tubes were then sealed as quickly as possible. Exposure for a few minutes frequently resulted in an appreciably lower m.p. The anhydrides were stored under vacuum in the preparation flask which was slowly vented through calcium chloride when material was to be removed.

(18) Ether was distilled from phosphorus pentoxide¹ and stored over sodium. Benzene was dried over sodium.

Reaction with Thiols (a) Preparation of Phenyl Benzenethiolsulfonate.—Pyridine (3.60 ml., dried over potassium hydroxide) was added to 13.32 g. of benzenesulfonic anhydride dissolved in 50 ml. of dry benzene in a flask protected from moisture. A solution of 4.14 g. of thiophenol in 50 ml. of benzene was then added during two hours with stirring. Stirring was continued for two hours, and the benzene solution was then washed with water, 70 ml. of cold 5% aqueous sodium hydroxide, and again with water until neutral. Concentration at a temperature below 55° of the solution dried over anhydrous magnesium sulfate gave 9.73 g. of a yellow oil which soon darkened. The oil upon rubbing with several small portions of ice-cold petroleum ether gave 6.84 g. (73%) of a black oily solid, an ethanol solution of which was boiled briefly with Darco, filtered and adjusted to incipient turbidity with water at 40°. The solution, after decantation from a small amount of tar and seeding, gave 3.61 g. (38%) of the thiolsulfonate as tan prisms, m.p. 44.5–45.5°. Saponification, extraction with benzene, and acidification gave a crystalline precipitate which easily dissolved in more water and gave a voluminous precipitate with ferric chloride solution,¹⁹ as expected of benzenesulfonic acid.

After several recrystallizations from ethanol, large ivory-colored tablets were obtained having a constant m.p. of 45–46°; m.p. reported,²⁰ 45°.

Anal. Calcd. for $C_{12}H_{10}O_2S_2$: C, 57.57; H, 4.03. Found: C, 57.70; H, 4.11.

A reaction carried out as described except for addition and subsequent stirring at the reflux temperature, as suggested⁶ for the reaction of sulfonyl chlorides and thiols, resulted in a 25% yield of the thiolsulfonate, m.p. 44–45°, and 17% of diphenyl disulfide, m.p. 59.5–60.5°, undepressed by authentic material.

(b) **Preparation of *p*-Tolyl *p*-Toluenethiolsulfonate.**—This ester was prepared in a manner similar to that first described above (except that the times of addition and stirring were each extended about one hour), using 3.8 ml. of pyridine, 15.21 g. of *p*-toluenesulfonic anhydride and 4.80 g. of *p*-thiocresol. After washing the oily tan solid (11.22 g.) with petroleum ether, 9.88 g. (92%) of tan powder was obtained, m.p. 68–72°. Recrystallization from aqueous ethanol of the solid obtained from the evaporated petroleum ether gave 0.76 g. (16%) of di-*p*-tolyl disulfide, m.p. 45.0–46.0°, undepressed by authentic material.

Recrystallization of the thiolsulfonate (5.93 g.) from aqueous ethanol, with decantation from tar, yielded 4.56 g. (71%) of nearly colorless translucent rhomboidal tablets, m.p. 78–79°, which upon further recrystallization from ethanol gave material having a constant m.p. of 78.5–79.5°; m.p. reported,²¹ 76°, 78°. Saponification and treatment with ferric chloride solution confirmed the presence of the sulfonic acid moiety.

Anal. Calcd. for $C_{14}H_{14}S_2O_2$: C, 60.40; H, 5.07. Found: C, 60.23; H, 4.84.

Reaction with Pyridine.—A solution of 9.5 g. of dry pyridine in 100 ml. of benzene was added to 17.9 g. of benzenesulfonic anhydride dissolved in 200 ml. of dry benzene. Dry ether (550 ml.) was added, and the resulting suspension allowed to stand at –5° for several days. The solvent was removed using a filter stick, and the solid swirled with benzene and then ether at room temperature; most of the solid redissolved. The residual solid, which seemed to be largely pyridinium benzenesulfonate, amounted to 2.5 g. Recrystallization from ethylene chloride gave 1.8 g. of hygroscopic tan platelets, m.p. 125–130°; m.p. reported,²² 130–133°; neut. equiv., 243 (calcd., 237).

Concentration of the original filtrate and washes gave 21.5 g. (95%, assuming a 1:1 complex of the anhydride and pyridine) of very hygroscopic cream-colored powder, m.p. 92–110°; hydrolysis equiv., 215 (calcd., 189). Two recrystallizations from dry ethylene chloride gave 9.4 g. (42%) of extremely hygroscopic small tan rods, m.p. 96–114° (sealed tube, rise of 2°/min. from 78°). The solid

(19) L. Ackerman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 243 (1946).

(20) E. Knoevenagel and A. Römer, *Ber.*, **56**, 215 (1923).

(21) Beilstein, "Handbuch der Organischen Chemie," Vol. 11, 4th ed., 2nd supplement, Springer-Verlag, Berlin, 1950, p. 70. The m.p. 87–88° also here reported is presumably an error.

(22) E. Gebauer-Fülnegg and F. Riesenfeld, *Monatsh.*, **47**, 185 (1926).

was readily soluble in water, except for a small amount of impurity, giving a strongly acidic solution. After neutralization a strong odor of pyridine was evident; hydrolysis equiv., 199 (calcd. for the 1:1 complex, 189).

A solution of 2.93 g. of phenol in 10 ml. of dry benzene was added to 7.60 g. of the complex in 15 ml. of benzene. The mixture was allowed to stand with occasional swirling for two days, and was then heated for one-half hour under reflux. Combined benzene extracts were washed twice with cold 10% aqueous sodium hydroxide and then with water until neutral. Concentration of the solution dried over anhydrous magnesium sulfate gave 4.11 g. (87%) of phenyl benzenesulfonate as a friable nearly colorless solid, m.p. 34.5–35.5°, undepressed by an authentic sample.²³

Friedel-Crafts Type Reactions (a) Preparation of Diphenyl Sulfone.—A suspension of 14.85 g. of anhydrous aluminum chloride in 50 ml. of dry benzene was cooled to 5° and 15.38 g. of benzenesulfonic anhydride in 100 ml. of dry benzene was added during 30 minutes with good stirring at 5–10°. A mildly exothermic reaction occurred, and hydrogen chloride was slowly evolved. The mixture was stirred at 5° for one hour, after which the bath was removed and stirring continued for two hours and then for one-half hour at the reflux temperature. The cooled mixture was poured onto ice and 30 ml. of concentrated hydrochloric acid. Combined benzene extracts were washed with water until neutral and dried over anhydrous magnesium sulfate. Concentration gave 11.12 g. (99%) of pale-yellow platelets, m.p. 124.5–125.5°. Recrystallization from ethanol gave 10.42 g. (93%) of nearly colorless rhomboidal tablets, m.p. 125.5–126°, undepressed by an authentic sample.²⁴

(b) Preparation of Phenyl *p*-Bromophenyl Sulfone.—Aluminum chloride (12.3 g.) was added during one-half hour to 12.47 g. of benzenesulfonic anhydride in 30 ml. of bromobenzene with stirring. Occasional cooling was applied to maintain the temperature at about 30° until the mixture became gelatinous, when it was warmed briefly until it could be stirred. The mixture was stirred without further heating for one hour and then at 75–85° for four hours. The cooled mixture was poured onto ice and 25 ml. of concentrated hydrochloric acid, and then steam distilled until 600 ml. of distillate was collected. Benzene extracts of the undistilled residue were washed until neutral, dried over anhydrous magnesium sulfate, treated with Darco and concentrated; yield 11.26 g. (91%) of slightly oily solid, m.p. 87–105°. Recrystallization from ethanol gave 9.18 g. (74%) of phenyl *p*-bromophenyl sulfone, m.p. 105.5–108°. Recrystallization from ethanol and petroleum ether-benzene mixtures raised the m.p. to a constant value of 108.5–109.5°; m.p. reported,²⁵ 108–108.5°. Derivatization as the dinitrosulfone²⁷ gave pale-yellow acicular prisms having a constant m.p. of 164–165°; reported, 162–163°.

Malonic Ester Type Synthesis. Preparation of Diethyl Phenylsulfonylmalonate.²⁸—Diethyl ethoxymagnesiummalonate²⁹ was prepared by adding one-fourth of a solution of

(23) Prepared in 94% yield, using pyridine as a base, by a method based on those of J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 273 (1912), and F. Reverdin and P. Crepeux, *Ber.*, **35**, 1439 (1902).

(24) Prepared by modification of a reported procedure.⁷ Benzenesulfonyl chloride (100 g.) in 200 ml. of benzene was added with stirring to 90.6 g. of aluminum chloride in 300 ml. of benzene during one hour at 40–46°. The mixture was heated under reflux for one hour, and then chilled and poured onto ice and 80 ml. of concentrated hydrochloric acid. A benzene extract was washed until neutral, dried and concentrated; yield 86.0 g. (70%), m.p. 121–123°. Two recrystallizations from ethanol gave colorless rhomboidal tablets (59%). m.p. 125.5–126.5°. Both this sample and that from the anhydride sometimes had m.p. 129–130°; diphenyl sulfone has been reported to exist in two forms, m.p. 124 and 128°.²⁵

(25) V. J. Mikeska, N. T. Farinacci and M. T. Bogert, *THIS JOURNAL*, **58**, 1869 (1936).

(26) S. C. J. Olivier, *Rec. trav. chim.*, **33**, 116 (1914).

(27) C. A. Buehler and J. E. Masters, *J. Org. Chem.*, **4**, 262 (1939).

(28) Jackson and Whitmore⁹ obtained this compound as a by-product in unstated yield, and characterized it only as the sodium salt.

(29) H. Lund, A. U. Hansen and A. F. Voigt, *Kgl. Danske Videnskab. Selskab. Mat. fys. Medd.*, **12**, No. 9, 23 pp. (1933) [*Chem. Centr.*, **105** I, 1961 (1934)]; H. Lund, *Ber.*, **67**, 935 (1934); H. Lund and A. F. Voigt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 594.

8.79 g. of diethyl malonate in 8.5 ml. of rigorously dried ethanol³⁰ to a mixture of 1.39 g. of magnesium turnings and 0.1 ml. of carbon tetrachloride and, after reaction began, completing the addition during 10 minutes with stirring and occasional cooling. The mixture was heated at 80–90° with stirring for two hours, after which 200 ml. of dry benzene was added during 3.5 hours while solvent was removed by distillation with stirring. When the volume was 15 ml., 13.66 g. of benzenesulfonic anhydride in 30 ml. of benzene was added during 1.3 hours to the solution at the reflux temperature. Heating was continued for two hours, and the cooled mixture then hydrolyzed with water and 30 ml. of concentrated hydrochloric acid. Benzene extracts of the aqueous layer were washed until neutral and extracted with 10% aqueous sodium hydroxide. The basic extract was washed with benzene and acidified with 20 ml. of concentrated hydrochloric acid. An ether extract was washed with two 10-ml. portions of water, dried over anhydrous magnesium sulfate, and concentrated. There was obtained 7.32 g. (53%) of a nearly colorless friable solid, m.p. 38.5–43°; neut. equiv. (in alcohol, using phenolphthalein and standard sodium hydroxide), 279 (calcd., 300). Recrystallization from ether-petroleum ether (3:1), with careful cooling to prevent separation of oil, resulted in fine colorless crystals in 46% yield, m.p. 43.5–44.5°. Further crystallization gave material with a constant m.p. of 44.5–45.5°; neut. equiv. 303. An alcoholic solution gave a light orange color, slightly different from a blank, with 1% alcoholic ferric chloride solution.

Anal. Calcd. for C₁₃H₁₆O₈S: C, 51.99; H, 5.37. Found: C, 52.01; H, 5.14.

A mixture of the crude product (2.47 g.) with 40 ml. of 25% sulfuric acid was heated at the reflux temperature for about three hours until there was no further gas evolution, and then for one-half hour more. The mixture was then continuously extracted with 35 ml. of chloroform which was then dried over anhydrous magnesium sulfate and concentrated. The oil obtained (1.78 g.) was seeded, chilled in Dry Ice, and triturated with petroleum ether-ether (2:1); yield 1.54 g. (82%) of white powder, m.p. 37.0–39.5°. Several recrystallizations from ether-petroleum ether mixtures gave colorless acicular prisms with a constant m.p. of 42.5–43.5°, undepressed by an authentic sample of ethyl phenylsulfonylacetate³¹; reported m.p. 45°.

Reaction with Grignard Reagents (a) Phenylmagnesium Bromide.—The phenylmagnesium bromide prepared in 50 ml. of ether from 1.70 g. of magnesium and 9.33 g. of bromobenzene was added to 14.65 g. of benzenesulfonic anhydride in 150 ml. of dry toluene during 45 minutes with vigorous stirring while the temperature was maintained at –30 to –20°. The mixture was stirred at –30 to –20° for two hours, after which a weak Gilman test³² was obtained which became negative after removal of the bath and continuation of stirring for three hours. Water and 1 *N* hydrochloric acid were then added and the aqueous layer was extracted with ether.

The aqueous layer was neutralized, filtered and concentrated to dryness. The solid was heated with phosphorus pentachloride and a benzene extract shaken with concentrated ammonium hydroxide. The solid obtained by concentration and acidification of the aqueous layer was recrystallized from water and gave 0.61 g. (8%) of benzenesulfonamide, m.p. and mixture m.p. 153.5–154.5°.

The ether extract was then washed with aqueous potassium bicarbonate and water which were acidified and extracted with ether. The ether solution was washed with a little water, dried over anhydrous magnesium sulfate and concentrated. The benzenesulfonic acid obtained (2.46 g., 35%; m.p. 76–79.5°) was reprecipitated from basic solution and gave 2.08 g. (30%) of fine colorless crystals, m.p. 75–77.5°, undepressed by an authentic sample; the product instantly decolorized aqueous solutions of potassium permanganate and bromine.

The ether extract was next extracted with cold 10% aqueous sodium hydroxide and with water until neutral.

(30) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 359; prepared by the diethyl phthalate method.

(31) A. Michael and A. M. Comey, *Am. Chem. J.*, **5**, 116 (1883).

(32) Ref. 30, p. 408.

The combined aqueous layers were washed with ether, acidified, and extracted with benzene which after washing, drying and concentration yielded 0.09 g. (2%) of phenol, identified as tribromophenol, m.p. 92–94°; reported,³³ 95°.

The ether extract was then dried over anhydrous magnesium sulfate and concentrated to an oily solid (4.78 g.) which upon trituration with petroleum ether–ether (3:1) gave 2.19 g. (20%) of diphenyl sulfone, m.p. 118–123°. Recrystallization from ethanol gave 1.78 g. (17%) of tan rhomboidal plates, m.p. 125.5–126°, undepressed by an authentic sample.²⁴

The petroleum ether–ether extract upon concentration gave 2.28 g. of an intractable oil from which no phenyl benzenesulfonate could be isolated either by seeding and prolonged cooling, or as the nitro derivative.

(b) **Phenylethynylmagnesium Bromide.**—Phenylacetylene (6.41 g.) was added to the ethylmagnesium bromide prepared in 50 ml. of ether from 6.9 g. of ethyl bromide and 1.6 g. of magnesium, and after standing for 1.5 hours the mixture was heated under reflux for two hours. Benzene (25 ml.) was added, and the 0.0616 mole of phenylethynylmagnesium bromide present³⁴ was added to 16.93 g. of benzenesulfonic anhydride in 50 ml. of dry benzene during one hour with stirring, after which a negative Gilman test³² was obtained. After heating at the reflux temperature for 4.5 hours and cooling, water and 1 *N* hydrochloric acid (65 ml.) were added. A benzene extract of the mixture was washed with aqueous sodium bicarbonate, which on faint acidification gave a copious precipitate with ferric chloride solution indicating the presence of a sulfonic acid,¹⁹ and was then dried over anhydrous magnesium sulfate and concentrated to a red-brown oil; yield 8.63 g. (84% of phenylethynyl bromide). The oil (7.42 g.) upon distillation using an 8-cm. modified Claisen head gave 3.14 g. (36%) of yellow oil, b.p. 77–81° (7 mm.), n_D^{25} 1.6057–1.6068. Redistillation gave a pale yellow oil, b.p. 79–79.5° (7 mm.), n_D^{25} 1.6066; b.p. reported for phenylethynyl bromide, 84–85° (10 mm.).³⁵ There was a large residue in both distillations (*cf.* ref. 36). The product had a bromine content of 41.43% (calcd., 44.15%); it darkened considerably on standing. Unlike phenylacetylene, it gave no precipitate with ammoniacal silver nitrate solution, but after reduction³⁶ with zinc dust in ethanol gave a voluminous precipitate soluble in dilute nitric acid.

The product was converted³⁶ to ω -bromoacetophenone in 37% yield, m.p. 48.5–50°. Recrystallization from ether–petroleum ether gave lachrymatory colorless plates having a constant m.p. of 49.5–51°; m.p. reported,³⁶ 52–54°.

(33) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 230.

(34) Ref. 30, p. 407.

(35) C. J. Wilson and H. H. Wenzke, *THIS JOURNAL*, **56**, 2026 (1934).

(36) J. U. Nef, *Ann.*, **308**, 310 (1899).

Reaction with Sodium Sulfite. Preparation of Benzenesulfonic Acid.—Benzenesulfonic anhydride (9.97 g.) was quickly ground and added to 8.5 g. of sodium sulfite in 30 ml. of water. The mixture was warmed at 44–50° during two hours with good stirring, and a few milliliters of saturated sodium carbonate solution was added from time to time to maintain slight alkalinity. It was then heated to boiling, and after filtration the ice-cold filtrate was strongly acidified with about 14 ml. of concentrated hydrochloric acid. The resulting solid was extracted into six 15-ml. portions of ether which were combined and extracted with 17 ml. of cold 15% aqueous sodium hydroxide. The aqueous layer after acidification with 6.3 ml. of concentrated hydrochloric acid was extracted with ether, and the extract dried over anhydrous magnesium sulfate and concentrated below 38°; yield of slightly oily benzenesulfonic acid, 2.93 g. (62%), m.p. 66.5–77°; neut. equiv. 155 (calcd., 142). Recrystallization from water gave a colorless crystalline solid, still somewhat oily, m.p. 69.5–75°, undepressed by authentic material (m.p. 77.5–79°); neut. equiv., 159. The product decolorized aqueous potassium permanganate and bromine solutions instantly. Partial decomposition appeared to occur during the attempted purification.

Reaction with Hydrogen Bromide.—Benzenesulfonic anhydride (19.5 g.) was heated at 94–97° with vigorous stirring while hydrogen bromide was passed into the liquid rapidly for 3.5 hours, then slowly for three hours. After the mixture had stood for 40 hours, extraction of the solid with petroleum ether and benzene left a considerable amount of hygroscopic residue (presumably benzenesulfonic acid), a water solution of which was extracted with benzene. The combined organic extracts were washed with aqueous potassium bicarbonate, dried over anhydrous magnesium sulfate and concentrated to 9.28 g. of waxy solid which after recrystallization from petroleum ether gave 6.97 g. (57%) of bis-(*p*-bromophenyl) disulfide, m.p. 86–92°. A second recrystallization gave 5.77 g. (47%), m.p. 92.5–93.5°, and further recrystallization from petroleum ether and cyclohexane gave nearly colorless laths having a constant m.p. of 93.5–94.5°, undepressed by an authentic sample³⁷ (m. p. 94–95°).

Anal. Calcd. for $C_{12}H_8Br_2S_2$: C, 38.32; H, 2.14; Br, 42.50; S, 17.05. Found: C, 38.40; H, 2.21; S, 16.40; Br, 42.28.

A solution of the product in concentrated sulfuric acid at 120–150° had a deep indigo-blue color which disappeared on pouring into water.³⁸ Reduction³⁹ with zinc dust in methanol–hydrochloric acid gave *p*-bromothiophenol, m.p. 72–74°; m.p. reported 75°.

NASHVILLE 4, TENN.

RECEIVED JULY 5, 1951

(37) J. Toussaint, *Bull. soc. chim. Belg.*, **54**, 346 (1945).

(38) E. Baumann and C. Freusse, *Z. physiol. Chem.*, **6**, 321 (1881).

(39) E. Bourgeois and A. Abraham, *Rec. trav. chim.*, **30**, 422 (1911).