Conversion of 3-Hydroxydamsin (3) to 4.—A solution of 13 mg of **3** in 10 ml of methylene dichloride was mixed with 2 g of thin layer silica gel G and dried. After 8 days, the silica gel was eluted with methanol. An nmr analysis of the syrup obtained on evaporating the methanol indicated a 1:1 mixture of **3** and **4**. The compounds were separated on a column of thin layer silica gel. Elution of the column with ether gave initially a fraction which yielded 3 mg of **3** and a later fraction which afforded 4 mg of **4**. Both compounds were obtained crystalline and were identical by tlc, nmr, and melting point with the materials previously isolated.

Synthesis of 4.—A solution of damsin (**5**, 110 mg) and trimethylaniline perbromide (167 mg, 1 equiv) in 10 ml of tetrahydrofuran was allowed to stand at room temperature. The crystals of trimethylaniline bromide which formed were filtered and the filtrate was concentrated to a syrup. Nmr analysis of the crude syrup indicated a 1:1 mixture of damsin and another compound, presumably 3-bromodamsin. The syrup was dissolved in 5 ml of dimethyl sulfoxide and mixed with 5 ml of 0.75 *N* potassium hydroxide. After the solution had warmed for 1 hr on a steam bath, it was acidified with hydrochloric acid and extracted with chloroform. The syrup obtained on evaporating the chloroform was chromatographed over silica gel. Elution of the column with ether afforded first damsin, then damsin mixed with **4**, and finally fractions containing **4**. The latter fractions afforded 15 mg of crystals, mp 147–148°, which were identical with authentic material by melting point, mixture melting point, and nmr and infrared spectra. 3-Hydroxydamsin (**3**) was not detected by nmr or tlc in any fractions from the column.

Synthesis of 3-Hydroxydamsin (3).—Ambrosiol (**6**, 0.5 g, 1.9 mmoles), pyridinium trifluoroacetate (0.1 g), pyridine (0.5 ml), and acetic anhydride (0.3 ml, 3.0 mmoles) were dissolved in 4 ml of dimethyl sulfoxide. After 24 hr at room temperature, the reaction solution was diluted with 25 ml of water and extracted three times with 20-ml portions of chloroform. The combined extracts were dried and concentrated to a syrup. Nmr analysis of the syrup indicated 10% starting material, 13% 3-hydroxydamsin, 64% **7**, and 13% **8**. The mixture was chromatographed over silica gel using first chloroform and later chloroform–ether as eluents. Nmr analysis of the syrups obtained on concentration of the solvent revealed that the first fractions were nearly pure **7**. Later fractions contained mixtures which were mainly **8** and **7**, then **8** and **3**, and finally **3** and **6**. The fractions which contained mostly **3** were combined and rechromatographed over silica gel by eluting with chloroform yielding finally 15 mg of pure crystals which were identical with the natural product by melting point, mixture melting point, infrared, and nmr.

The fractions from the first column which were nearly pure **7** were combined and rechromatographed over silica gel using ether as the eluting solvent. The first cuts afforded a clear, white syrup of **7** (0.1 g), pure by tlc (R_f 0.8 on tlc plates developed in ether) and nmr: ultraviolet (MeOH), λ_{max} 209 mμ (ϵ ~8000) and 309 (35); infrared ($CHCl_3$), 3400 (hydroxyl), 1750 (ketone and lactone), and 1650 cm^{-1} (double bond).

Fractions of the first column which contained mostly **8** with a little **7** yielded crystalline **8** on trituration under ether. The crystals which were obtained (20 mg) were sublimed (180°, 0.1 mm of Hg) to give pure **8**: mp 232–233°; ultraviolet (MeOH), λ_{max} 210 mμ (ϵ 9000) and 260 (6600); infrared (Nujol mull), 3200 (hydroxyl), 1700 (conjugated ketone), 1725 (lactone), and 1630 cm^{-1} (double bond).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; O, 24.40. Found: C, 68.88; H, 6.96; O, 24.19; mol wt (mass spectrum), 262.

Registry No.—**3**, 13250-08-3; **4**, 13250-09-4; **7**, 13250-10-7; **8**, 13250-11-8.

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The Synthesis of Aryl Sulfones

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There are several methods of synthesizing aromatic sulfones, but many of these either give low yields, have serious limitations, or require special techniques.[1]

The most practical laboratory method of preparing aryl sulfones is a Friedel–Crafts method employing a sulfonyl chloride, aromatic hydrocarbon, and aluminum chloride catalyst[2] (eq 1). The yields in this reaction

$$ArSO_2Cl + Ar'H \xrightarrow[AlCl_3]{} ArSO_2Ar' + HCl \qquad (1)$$

are generally satisfactory and range from 60 to 90%.

The oxidation of sulfides and sulfoxides by a variety of oxidizing agents also yields sulfones.[1] The displacement reaction between a sodium sulfinate and an aryl halide gives good yields of aromatic sulfones, but only in the case when strong electron withdrawing groups, such as nitro, are present in the aromatic ring of the halide. Gilman[3] has reported the synthesis of aryl sulfones by the reaction of Grignard reagents with aryl-*p*-toluene sulfinates. The yields vary in this synthesis from 40–80%.

Other preparative methods have involved the removal of water between an aryl sulfonic acid and an aromatic hydrocarbon by some dehydrating agent or at high temperatures as illustrated by reaction 2. Meyer[4]

$$ArSO_3H + Ar'H \xrightarrow[\Delta]{} ArSO_2Ar' + H_2O \qquad (2)$$

prepared several aromatic sulfones by passing the vapor of an aromatic hydrocarbon through a molten solution of a sulfonic acid in the temperature range of 125–200°. The yields in this preparation are low, 30–40%, and often times mixtures of sulfones are obtained through trans-sulfonation reactions. Drews[5] and co-workers found a major complication in this direct condensation reaction which resulted from the desulfonation of the molten sulfonic acid at high temperature. For example, toluene and *p*-xylenesulfonic acid gave not only the expected *p*-tolyl-*p*-xylyl sulfone but also di-*p*-tolyl sulfone and di-*p*-xylyl sulfone. These results cast some doubt on the properties of specific isomers reported in the original work by Meyer,[4] since he was unaware of the above complications.

Another method to effect reaction 2 above has been reported in the early work by Michael and Adair.[6] These investigators used phosphorus pentoxide as the dehydrating agent and obtained sulfones, but only in rather low yields.

In a previous study of the Jacobsen rearrangement of aryl sulfonic acids in polyphosphoric acid,[7] it was observed that sulfones were produced when certain

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(1) For a review of the older methods of preparing sulfones, see C. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p 658.

(2) H. Beckurts and R. Otto, *Ber.*, **11**, 472, 2066 (1878).

(3) H. Gilman, *et al.*, *J. Am. Chem. Soc.*, **47**, 2047 (1925).

(4) A. Meyer, *Ann.*, **433**, 327 (1923).

(5) H. Drews, S. Meyerson, and E. Fields, *J. Am. Chem. Soc.*, **83**, 3871 (1961).

(6) A. Michael and A. Adair, *Ber.*, **10**, 583 (1877).

TABLE I

AROMATIC SULFONES PREPARED IN POLYPHOSPHORIC ACID AT 80°[a]

Starting materials		Reaction time, hr	Sulfone product, RSO_2R'		Registry no.	% yield	Obsvd mp, °C	Lit. mp, °C
R in RSO_3H	Aromatic hydrocarbon		R	R'				
C_6H_5	Benzene	24	C_6H_5	C_6H_5	127-63-9	23	121	123[b]
C_6H_5	Toluene	8	C_6H_5	p-$CH_3C_6H_4$	640-57-3	44	122	125[c]
C_6H_5	*m*-Xylene	8	C_6H_5	2,4-$(CH_3)_2C_6H_3$	4212-74-2	63	85	87[d]
C_6H_5	Mesitylene	7	C_6H_5	2,4,6-$(CH_3)_3C_6H_2$	3112-82-1	69	73	*e*
C_6H_5	Naphthalene	8	C_6H_5	α-$C_{10}H_7$	13249-96-2	49[f]	98	98[b]
C_6H_5	Biphenyl	8	C_6H_5	p-C_6H_5-C_6H_4	1230-51-9	15[f]	147	148[c]
p-$CH_3C_6H_4$	Benzene	8	p-$CH_3C_6H_4$	C_6H_5	. . .	22	125	125[c]
p-$CH_3C_6H_4$	Chlorobenzene	8	. . .	. . .	. . .	0	. . .	. . .
p-$CH_3C_6H_4$	Toluene	8	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	599-66-6	47	156	158[g]
p-$CH_3C_6H_4$	*m*-Xylene	8	p-$CH_3C_6H_4$	2,4-$(CH_3)_2C_6H_3$	3249-97-3	77	49	51[h]
p-$CH_3C_6H_4$	Mesitylene	9	p-$CH_3C_6H_4$	2,4,6-$(CH_3)_3C_6H_2$	15184-64-5	94	117	119[b]
p-$CH_3C_6H_4$	Naphthalene	8	p-$CH_3C_6H_4$	α-$C_{10}H_7$	13249-99-5	47[f]	119	121[b]
2,4-$(CH_3)_2C_6H_3$ (Na salt)	*m*-Xylene	8	2,4-$(CH_3)_2C_6H_3$	2,4-$(CH_3)_2C_6H_3$	5184-75-8	82	120	121[i]
2,4-$(CH_3)_2C_6H_3$ (Na salt)	Mesitylene	8	2,4-$(CH_3)_2C_6H_3$	2,4,6-$(CH_3)_3C_6H_2$	13250-01-6	82	155[j]	156[k]
2,5-$(CH_3)_2C_6H_3$	*p*-Xylene	4	2,5-$(CH_3)_2C_6H_3$	2,5-$(CH_3)_2C_6H_3$	6632-44-6	50	143	142[i]
α-$C_{10}H_7$	Naphthalene	8	α-$C_{10}H_7$	α-$C_{10}H_7$	13250-03-8	55[f]	185[j]	187[b]
β-$C_{10}H_7$	Naphthalene	8	β-$C_{10}H_7$	α-$C_{10}H_7$	13250-04-9	54[f]	119[j]	121[b]
β-$C_{10}H_7$	*m*-Xylene	8	β-$C_{10}H_7$	2,4-$(CH_3)_2C_6H_3$	13250-05-0	72	129[j]	128[b]
β-$C_{10}H_7$	Toluene	8	β-$C_{10}H_7$	p-$CH_3C_6H_4$	13250-06-1	50	154[j]	154[b]
2,4,5-$(CH_3)_3C_6H_2$	Benzene	24	2,4,5-$(CH_3)_3C_6H_2$	C_6H_5	13250-07-2	10	159	160[b]
2,4,6-$(CH_3)_3C_6H_2$	Mesitylene	8	2,4,6-$(CH_3)_3C_6H_2$	2,4,6-$(CH_3)_3C_6H_2$	3112-79-6	80	201	202[k]

[a] All reactions contained 0.02 mole each of sulfonic acid and aromatic hydrocarbon in 60 g of polyphosphoric acid. [b] See reference 4. [c] C. A. Buehler and J. Masters, *J. Org. Chem.*, **4,** 262 (1939). [d] W. Steinkopf and R. Hubner, *J. Prakt. Chem.*, **141,** 193 (1934). [e] See comparison with Friedel–Crafts product in Experimental Section. [f] The product and unreacted aromatic hydrocarbon were separated by ether extraction. The sulfone was relatively insoluble in ether. [g] R. Otto, *Ber.*, **12,** 1177 (1879). [h] H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 887 (1955). [i] J. Pollok, *et al.*, *Monatsh*, **55,** 358 (1930). [j] Recrystallized from acetic acid. All other products were recrystallized from 95% alcohol. [k] W. Truce and O. Norman, *J. Am. Chem. Soc.*, **75,** 6023 (1953).

arylsulfonic acids and aromatic hydrocarbons were heated together in this medium. Because of this initial observation it seemed advantageous to investigate this method as a new and better way to synthesize aromatic sulfones. It is the purpose of this paper to report the results of such an investigation.

Results and Discussion

Aromatic sulfones can be synthesized in good yield by heating and stirring together a mixture of an aromatic sulfonic acid and aromatic hydrocarbon in a polyphosphoric acid (PPA) medium. The reactions were run at 80° for about 8 hr in most cases. No attempt was made to determine the optimum temperature and reaction time for each individual synthesis.

The reaction appears to have some advantages over the previous methods of preparing sulfones. The starting materials are more easily obtained. The isolation of the product is extremely simple and gives a much purer product than the Friedel–Crafts method. After reaction is complete the hot mixture is poured into ice water, whereupon the white sulfone precipitates from the solution and the PPA dissolves in the water. The crude solid sulfone is then filtered from the solution.

Table I contains the results that were obtained in the several preparations. The yields seem to be generally quite respectable considering the small amounts used and the fact that no attempt was made to isolate additional product from the mother liquor after recrystallization.

A mixture of isomers was formed in most of those cases in which the *ortho-* and *para-*directing effects of the groups on the benzene ring would orient the sulfone bond into more than one position. The results recorded in Table I refer to the yield of the pure isomer obtained after recrystallization. No attempt was made to isolate or identify the other minor isomeric products.

The various isomers were identified chiefly from the comparison of melting points recorded in the literature. Infrared spectra of the compounds in Table I were also used for identification. Infrared analysis of the products showed two strong absorption bands at 1300–1350 and 1140–1160 cm^{-1} which are characteristic of the sulfone group.

Some of the work by Meyer[4] is of questionable reliability since evidently desulfonation and transsulfonation reactions occurred under his reaction conditions. In the present investigation it was important to know whether desulfonation of the aromatic sulfonic acid occurs at 80° in PPA. It was found that only mesitylenesulfonic acid desulfonated slightly upon heating in PPA at this temperature. A small amount of dimesityl sulfone was isolated from the reaction mixture. The more facile desulfonation of a sterically hindered acid like mesitylenesulfonic acid is in agreement with studies on the influence of structure on the ease of desulfonation of aromatic sulfonic acids.[8]

The reactivity of the aromatic hydrocarbon toward electrophilic substitution has a great influence on the ease of formation of the aryl sulfones listed in Table I. Polyalkylated benzenes appear to react more readily and give higher yields of product. The yields of aryl sulfones decreased as the number of methyl groups on benzene were reduced which gives the following relative

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(7) E. Marvell and B. Graybill, *J. Org. Chem.*, **30,** 4014 (1965).

(8) E. E. Gilbert, "Sulfonation and Related Reactions," Interscience Publishers, Inc., New York, N. Y., 1965, p 430.

order of hydrocarbon reactivity: mesitylene > xylene > toluene > benzene.[9]

Deactivated benzene rings appear to be very resistent toward sulfone formation. Chlorobenzene and *p*-toluenesulfonic acid gave no sulfone product under the usual reaction conditions. No attempt was made toward finding a higher temperature at which reaction would occur.

The relative reactivities of the aromatic substrates are consistent with a mechanism involving attack on the aromatic ring by an electrophilic reagent. The attacking electrophile in this case must be weak and demands an electron rich ring. The reaction mechanism in the formation of aryl sulfones apparently involves the sulfonium cation, $ArSO_2^+$, which is very similar to the mechanism involved in the preparation of aromatic ketones in PPA *via* the acyl cation, $ArCO^+$.[10]

Field[11] has reported the synthesis of sulfonic anhydrides from the reaction of the acid with phosphorus pentoxide. Because of the similarity of conditions with the present investigation it is highly probable that the aromatic sulfonic anhydride is an intermediate in the reaction.

The sodium salt of *m*-xylenesulfonic acid was also used effectively in the synthesis of sulfones in polyphosphoric acid. This fact makes the preparation reaction of PPA very versatile and attractive from the standpoint of availability of a wider range of starting materials.

It was of some interest to see if the same or different isomers were obtained using the Friedel-Crafts synthesis of aromatic sulfones. In all the cases studied it was observed that the same sulfone isomer was isolated using the aluminum chloride method as in the synthesis with PPA.

Experimental Section

Materials.—The following chemicals were obtained commercially and used without further purification. Benzenesulfonic acid monohydrate, *p*-toluenesulfonic acid monohydrate, sodium 2,4-dimethylbenzenesulfonate, α-naphthalenesulfonic acid dihydrate, β-naphthalenesulfonic acid monohydrate, benzenesulfonyl chloride, *p*-toluenesulfonyl chloride, benzene, toluene, *m*-xylene, biphenyl, naphthalene, and chlorobenzene were all Eastman reagent grade. Mesitylene, pseudocumene, and *p*-xylene were Eastman practical grade. The polyphosphoric acid was Matheson reagent grade.

1,2,4-Trimethyl-5-benzenesulfonic acid was prepared according to the procedure of Smith and Cass.[12] Mesitylenesulfonic acid was synthesized by the direct sulfonation of mesitylene.[13] *p*-Xylenesulfonic acid dihydrate was prepared by the direct sulfonation of *p*-xylene with concentrated sulfuric acid: melting point of *p*-xylenesulfonic acid, 86° (lit.[14] mp 86°). The infrared spectra were run in carbon disulfide solution (12–15 mg/ml) on a Beckman IR-8 instrument.

Sulfone Synthesis in Polyphosphoric Acid.—Table I contains most of the pertinent data for the preparation of the various sulfones. The following procedure is presented as typical for the other preparations.

***p*-Tolyl-2,4-dimethylphenyl Sulfone.**—A mixture of 3.8 g (0.02 mole) of *p*-toluenesulfonic acid monohydrate, 2.1 g (0.02 mole) of *m*-xylene, and 60 g of polyphosphoric acid was placed in a stoppered round-bottom flask equipped with a mechanical stirrer and heated in an oil bath. After heating at 80° and stirring for 8 hr, the hot mixture was poured into ice water. Upon cooling and stirring, the thick liquid solidified. The crude white product was filtered from solution and recrystallized from ethanol. A second recrystallization from alcohol afforded 4.0 g (77 %) of white crystals which melted at 49° (lit.[15] mp 51°). The other possible isomeric product, *p*-tolyl-2,6-dimethylphenyl sulfone, melts at 121°.[15] An infrared spectrum of the product contained two strong absorption bands at 1160 and 1320 cm^{-1} which is indicative of the sulfone group.

Desulfonation of Mesitylenesulfonic Acid in PPA.—Mesitylenesulfonic acid (5 g, 0.021 mole) was heated and stirred in 60 g of polyphosphoric acid at 80° for 8 hr. After the reaction mixture was poured into water and allowed to sit overnight, 0.2 g of brown solid was filtered from solution. Recrystallization of the solid from acetic acid gave crystals of dimesityl sulfone, mp 202° (lit.[16] mp 202°). The melting point of the product mixed with authentic sample was undepressed.

Sulfone Synthesis with Aluminum Chloride. Phenyl Mesityl Sulfone.—Aluminum chloride (2.7 g, 0.02 mole) was added to 10 ml of mesitylene and 3.5 g (0.02 mole) of benzenesulfonyl chloride was added dropwise. The reaction flask was cooled as needed. After the addition was complete, the reaction solution was refluxed for 2 hr. The mixture was then poured into water and an additional 20 ml of benzene was added. The benzene layer was extracted twice with a bicarbonate solution and then washed with water. After drying, the benzene solution was concentrated and cooled to give crystals of the product. Recrystallization of the solid product from ethanol gave needles which melted at 74°. The yield was only 1.9 g. The infrared spectrum of this product was identical with that of the sulfone isolated in the PPA synthesis using benzenesulfonic acid and mesitylene. A mixture melting point of these two compounds was undepressed.

***p*-Tolyl-*m*-xylyl Sulfone.**—*p*-Toluenesulfonyl chloride (3.8 g, 0.02 mole), 2.7 g (0.02 mole) of aluminum chloride, and 10 ml of *m*-xylene were reacted together in the manner described above. An oil was obtained after evaporation of the organic extract. Recrystallization of the product from ethanol eventually yielded crystals which melted at 45°. Although this melting point was slightly lower than that of the product isolated from the PPA preparation, the infrared spectra of both compounds were identical.

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[9] The low yields in the case of benzene may also be due to its lower boiling temperature. At the temperature of the reaction (80°) benzene tended to vaporize from the reaction vessel. Benzene vapor tended to escape even when a sealed flask with magnetic stirrer was used.

[10] D. A. Shirley, "Organic Chemistry," Holt, Rinehart, and Winston, Inc., New York, N. Y., 1964, p 634.

[11] L. Field, *J. Am. Chem. Soc.*, **74**, 394 (1952).

[12] L. Smith and O. Cass, *ibid.*, **54**, 1617 (1932).

[13] C. Suter and A. Weston, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1946, p 162.

[14] O. Jacobsen, *Ber.*, **10**, 1009 (1877).

[15] See ref *h* in Table I.

[16] See ref *k* in Table I.

The Preparation of Spiro[3.4]oct-1-ene

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In the course of our work with 5-spiro-substituted cyclopentadienes, it had been noted that diene **1** dimerizes readily at room temperature, very much in contrast to its expectedly slow reaction with conventional

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[1] (a) Taken from the Ph.D. dissertation submitted by G. Whitney in partial fulfillment of the Cornell Graduate School requirements, 1966; (b) G. C. W. would like to acknowledge an NIH predoctoral fellowship for the years 1964–1966.