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### A DIRECT SYNTHESIS OF 2- AND 4-HYDROXYDIARYL SULFOXIDES

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## A DIRECT SYNTHESIS OF 2- AND 4-HYDROXYDIARYL SULFOXIDES

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A number of 2-hydroxydiaryl sulfoxides, as well as a few 4-hydroxy analogs, have been prepared in fair to good yields by the direct arylsulfonylation of substituted phenols in the presence of anhydrous aluminum chloride.

### INTRODUCTION

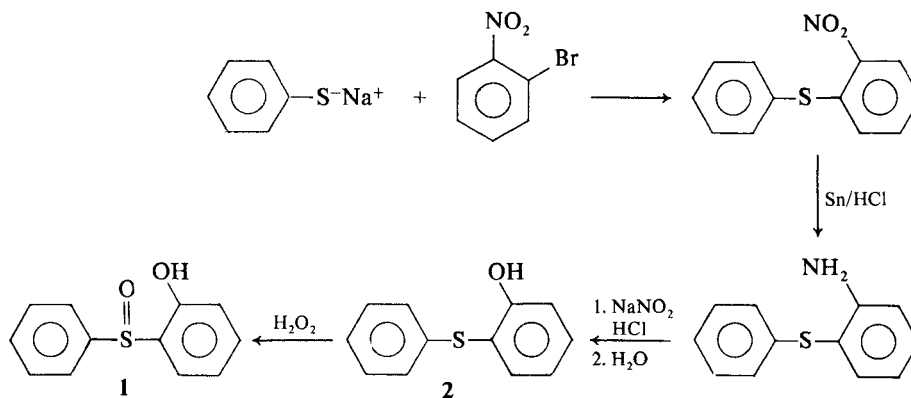
The 2-hydroxydiaryl sulfoxides (e.g., **1**) are an interesting class of compounds, particularly from the aspect that intramolecular hydrogen bonding between the hydroxyl and sulfinyl moieties is possible.<sup>1</sup> However, not many of these unsymmetric compounds have been reported, possibly due to the unavailability of a convenient synthesis. Bourgeois and Huber<sup>2</sup> have reported the synthesis of 2-hydroxydiphenyl sulfide (**2**), which can then be oxidized to the sulfoxide **1**<sup>3</sup> (Scheme 1). Alternatively, Hilbert and Johnson<sup>4</sup> prepared **2** by the method outlined in Scheme 2. Meyers<sup>5</sup> prepared the *p*'-NO<sub>2</sub> derivative of **1** from *p*-chloronitrobenzene and *o*-methoxythiophenol using steps similar to the first in Scheme 1 and the last in Scheme 2 followed by a subsequent oxidation with H<sub>2</sub>O<sub>2</sub>. However, if a variety of substituted 2-hydroxydiphenyl sulfoxides is desired, these methods will not suffice, as starting materials are not readily available, overall yields are

low due to the lengthy synthesis and a final oxidation to sulfoxide is still necessary.

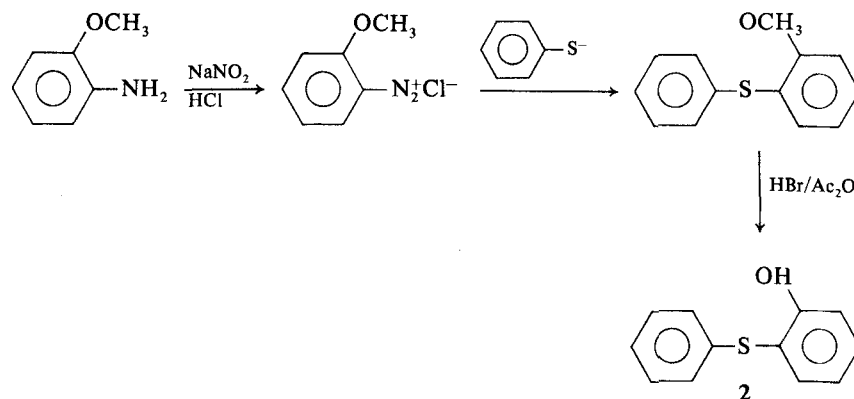
There have been several sporadic reports of Friedel-Crafts arylsulfonylation of simple and substituted aromatic hydrocarbons to form unsymmetric sulfoxides directly. Douglas<sup>6</sup> has reported that methylsulfonylation of benzene in the presence of anhydrous aluminum chloride forms methyl phenyl sulfoxide. It was reported that *p*-toluenesulfonyl chloride reacts with benzene/AlCl<sub>3</sub><sup>7</sup> and that benzenesulfonyl chloride reacts with azulene<sup>8</sup> to form unsymmetric sulfoxides, both in poor yields. Olah<sup>9</sup> reported the selectivity of the aluminum chloride-catalyzed *p*-toluenesulfonylation of benzene and polymethylbenzene with parasubstituted benzenesulfonyl chlorides in nitromethane.

### RESULTS AND DISCUSSION

We found it necessary to prepare a number of unsymmetric 2-hydroxydiaryl sulfoxides. The direct



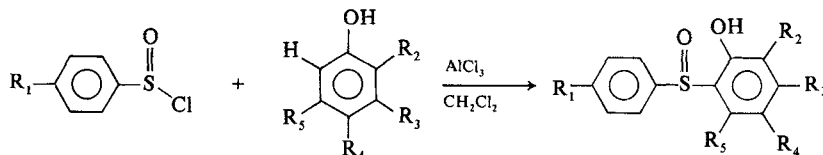
SCHEME 1



SCHEME 2

TABLE I

2-Hydroxydiaryl sulfides, along with pertinent data, formed by the following reaction:



Entry #	Compound					Yield %	mp(°C) (solvent) <sup>a</sup>	Analysis for	% Calculated % Found		
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>				C	H	S
1	H	H	H	CH <sub>3</sub>	H	64	135–137(EA)	C <sub>13</sub> H <sub>12</sub> O <sub>2</sub> S	67.21 67.71	5.21 5.22	13.80 13.57
2	H	H	H	C <sub>2</sub> H <sub>5</sub>	H	33	141–143(EA)	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub> S	68.26 68.02	5.73 5.69	13.02 13.19
3	H	H	H	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	H	55	130–131.5(EA)	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub> S	69.20 68.87	6.19 6.18	12.32 12.45
4	H	H	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	23	182–184(EA)	C <sub>16</sub> H <sub>18</sub> O <sub>2</sub> S	70.04 70.91	6.61 6.83	11.68 11.43
5	H	H	H	<i>t</i> -C <sub>5</sub> H <sub>11</sub>	H	43	104–120(EA)	C <sub>17</sub> H <sub>20</sub> O <sub>2</sub> S	70.80 70.38	6.99 6.62	11.12 11.59
6	H	H	H	<i>t</i> -C <sub>8</sub> H <sub>17</sub>	H	20	168.5–170.5(EA)	C <sub>20</sub> H <sub>26</sub> O <sub>2</sub> S	72.69 72.51	7.93 7.87	9.70 9.90
7	H	H	H	C <sub>6</sub> H <sub>5</sub>	H	31	155–156.5(EA)	C <sub>18</sub> H <sub>14</sub> O <sub>2</sub> S	73.44 72.84	4.79 4.86	10.89 10.70
8	H	CH <sub>3</sub>	H	CH <sub>3</sub>	H	58	97–99(EA)	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub> S	68.26 68.22	5.73 5.72	13.02 12.85
9	H	CH <sub>3</sub>	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	69	115–116.5(A)	C <sub>17</sub> H <sub>20</sub> O <sub>2</sub> S	70.80 71.00	6.99 7.30	11.12 10.91
10	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	CH <sub>3</sub>	H	75	66–72(EA)	C <sub>17</sub> H <sub>20</sub> O <sub>2</sub> A	70.80 70.64	6.99 6.87	11.12 11.11
11	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	28	90–95(E)	C <sub>20</sub> H <sub>26</sub> O <sub>2</sub> S	72.69 72.83	7.93 7.94	9.70 9.47
12	H	H	CH <sub>3</sub>	CH <sub>3</sub>	H	5	212–213(A)	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub> S	68.26 68.20	5.73 5.93	13.02 12.50
13	H	H	CH <sub>3</sub>	H	CH <sub>3</sub>	50 <sup>b</sup>	oil(EA) <sup>c</sup>	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub> S	68.26 68.40	5.73 5.73	13.02 12.75
14	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	45	180–183(E)	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub> S	68.26 67.89	5.73 5.84	13.02 12.61

TABLE I—continued

Entry #	Compound					Yield %	mp(°C) (solvent) <sup>a</sup>	Analysis for	% Calculated % Found		
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>				C	H	S
15	CH <sub>3</sub>	H	H	C <sub>2</sub> H <sub>5</sub>	H	68	120–122(EA)	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub> S	69.20 68.87	6.19 6.18	12.32 12.45
16	CH <sub>3</sub>	H	H	<i>t</i> -C <sub>3</sub> H <sub>7</sub>	H	60	122.5–124.5(EA)	C <sub>16</sub> H <sub>18</sub> O <sub>2</sub> S	70.04 70.42	6.61 6.66	11.68 11.92
17	CH <sub>3</sub>	H	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	69	162–165(A)	C <sub>17</sub> H <sub>20</sub> O <sub>2</sub> S	70.80 70.67	6.99 6.87	11.12 11.21
18	CH <sub>3</sub>	H	H	<i>t</i> -C <sub>5</sub> H <sub>11</sub>	H	34	132–134(A)	C <sub>18</sub> H <sub>22</sub> O <sub>2</sub> S	71.49 71.36	7.33 7.45	10.60 10.78
19	CH <sub>3</sub>	H	H	<i>t</i> -C <sub>8</sub> H <sub>17</sub>	H	47	155–157(A)	C <sub>21</sub> H <sub>28</sub> O <sub>2</sub> S	73.21 72.92	8.19 8.26	9.31 9.45
20	CH <sub>3</sub>	H	H	C <sub>6</sub> H <sub>5</sub>	H	66	175–182(M)	C <sub>19</sub> H <sub>16</sub> O <sub>2</sub> S	74.00 73.71	5.23 5.14	10.40 10.37
21	CH <sub>3</sub>	CH <sub>3</sub>	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	78	127–129(A)	C <sub>18</sub> H <sub>22</sub> O <sub>2</sub> S	71.49 71.38	7.33 7.13	10.60 10.73
22	CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	CH <sub>3</sub>	H	73	129–130(H)	C <sub>18</sub> H <sub>22</sub> O <sub>2</sub> S	71.49 71.39	7.33 7.25	10.60 10.92
23	CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	66	113–115(M)	C <sub>21</sub> H <sub>28</sub> O <sub>2</sub> S	73.21 73.08	8.19 8.12	9.31 9.51
24	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	H	CH <sub>3</sub>	H	32	184.5–192(E)	C <sub>17</sub> H <sub>20</sub> O <sub>2</sub> S	70.80 71.32	6.99 7.22	11.12 11.37
25	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	H	C <sub>6</sub> H <sub>5</sub>	H	60	161–163(E)	C <sub>22</sub> H <sub>22</sub> O <sub>2</sub> S	75.39 75.33	6.33 6.20	9.15 9.46
26	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	78	146–148(M)	C <sub>21</sub> H <sub>28</sub> O <sub>2</sub> S	73.21 73.01	8.19 8.27	9.31 9.37
27	Cl	H	H	CH <sub>3</sub>	H	53	182–185(EA)	C <sub>13</sub> H <sub>11</sub> ClO <sub>2</sub> S <sup>d</sup>	58.54 58.69	4.16 4.16	12.02 12.00

<sup>a</sup> This is the solvent used to wash or recrystallize the crude product: EA = ethyl acetate, E = ethanol, A = acetone, M = methanol, H = hexane.

<sup>b</sup> The isomer resulting from *para* attack is reported in Table II.

<sup>c</sup> This compound was soluble in cold ethyl acetate and its isomer (Table II) was not.

<sup>d</sup> Calculated for chlorine, 13.29%; found, 13.18%.

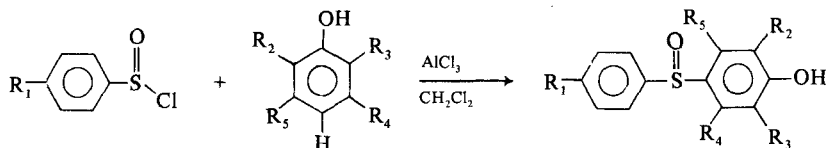
sulfonylation of phenols appeared to be the most direct route, particularly since substituted phenols are readily available commercially. The reaction of equivalent amounts of unsubstituted or *para*-substituted benzenesulfonyl chlorides, substituted phenols, and anhydrous aluminum chloride in methylene chloride near 0° for several hours, followed by a simple work-up and purification, led to fair to good yields of hydroxydiaryl sulfoxides (see Table I and II). In most examples, the crude product could be purified with a cold solvent wash, the major impurities being diaryl disulfides and residual phenols. No attempt was made to maximize the yields. All compounds exhibited infrared and nmr spectra consistent with the assigned structures (see Tables III and IV).

Sulfonylation should occur most readily at the *ortho* and *para* positions of phenols, since these positions are activated toward electrophilic sub-

stitution by the resonance effect of the hydroxyl group. However, when the *para* position is blocked, substitution will occur only at the *ortho* position. The nmr spectral data in Table III reflect this pattern of substitution. All compounds substituted only in the 5 position exhibit in the nmr a doublet ( $J = 8\text{--}9.5$  Hz) upfield (6.72–6.98) from the remaining aromatic protons, indicative of the proton at position 3 coupled to the proton at position 4 and shielded by the adjacent hydroxyl group. Entry 4 in Table III also reflects a *para* coupling ( $J = 1$ ) of the proton at 3 with that at 6. Entries 14, 20, and 27 also exhibit *meta* coupling ( $J = 2\text{--}2.5$ ) between the 4 and 6 protons. To truly show that this *meta* coupling results from the 4 and 6 proton coupling in the assigned isomer shown and not from *meta* coupling in the alternate isomer, entries 9, 10, 11, 21, 22, and 23 (Table III), which possess alkyl substituents in both the 3 and 5 positions, exhibit *meta*

TABLE II

4-Hydroxydiaryl sulfoxides, along with pertinent data, formed by the following reaction:



Entry #	Compound					Yield (%)	mp(°C) (solvent) <sup>a</sup>	Analysis for	% Calculated % Found		
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>				C	H	S
1	H	H	H	CH <sub>3</sub>	CH <sub>3</sub>	46 <sup>b</sup>	138–139(EA) <sup>c</sup>	C <sub>14</sub> H <sub>14</sub> O <sub>2</sub> S	68.26 68.16	5.73 5.68	13.02 13.08
2	H	H	H	H	H	82	144–145.5(EA) <sup>d</sup>				
3	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	H	48	133–135(EA) <sup>e</sup>				
4	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	H	H	H	H	62	146–148(EA)	C <sub>16</sub> H <sub>18</sub> O <sub>2</sub> S	70.04 69.98	6.61 6.59	11.68 11.92
5	Cl	H	H	H	H	42	166–167.5(EA)	C <sub>12</sub> H <sub>9</sub> ClO <sub>2</sub> S <sup>f</sup>	57.03 56.43	3.59 3.52	12.69 13.02

<sup>a</sup> This is the solvent used to wash the crude product: EA = ethyl acetate, E = ethanol.<sup>b</sup> The isomer resulting from *ortho* attack is reported in Table I.<sup>c</sup> This compound was insoluble in cold ethyl acetate and its isomer (Table I) was soluble.<sup>d</sup> Lit. mp 143–144 (see Reference 3).<sup>e</sup> Lit. mp 131–134 (E. Mueller, H. B. Stegmann and K. Scheffler, *Ann.* **645**, 79 (1961)).<sup>f</sup> Calculated for chlorine, 14.03%; found, 13.89%.

coupling between the protons at 4 and 6. The alternative isomer here would not possess *meta* protons.

Whenever both the *ortho* and *para* positions are available to arylsulfonylation as in phenol, only the *para* isomer is formed (entries 2, 4, and 5, Table IV). However, arylsulfonylation of 3,5-dimethylphenol occurs at both the *ortho* and *para* positions (Table III, entry 13 and Table IV, entry 1). This suggests that a steric effect must be operative in the latter example. Meyers<sup>10</sup> has pointed out and corrected the confusion concerning the regioselectivity of the electrophilic attack of thionyl chloride and sulfur dichloride on 3,5-dimethylphenol, the former affording *ortho* and the latter *para* products. Our results substantiate that, *a priori*, it is not possible to generalize from one electrophile to another as to their regioselectivities with 3,5-dimethylphenol.

We found that the reaction of benzenesulfonyl chloride with an equivalent amount of *p*-methylphenol in the absence of or in the presence of a one-third equivalent of anhydrous aluminum chloride did not afford any product. Thus, an equivalent amount of aluminum chloride was used in all reactions.

Benzenesulfonyl chloride was found to be unreactive with *p*-chloro- or *p*-cyanophenol. The reaction of arenesulfonyl chlorides with alkoxy substituted phenols afforded isomers which are less easily assigned definitive structures based on the type of data obtained herein. These products will require further examination before complete structure analyses can be reported.

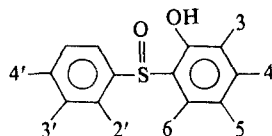
Since sulfoxides are easily oxidized to sulfones<sup>11</sup> and reduced to sulfides,<sup>12</sup> these classes of compounds would be readily accessible through the preparation of the sulfoxides described here.

A detailed discussion of the ir and nmr spectra with respect to intramolecular H-bonding will be submitted for publication in the future.

#### EXPERIMENTAL SECTION

The aromatic thiols and disulfides used in the preparation of the arenesulfonyl chlorides are available through Eastman Organic Chemicals or Aldrich Chemical Co., Inc. The arenesulfonyl chlorides were prepared according to the procedure of Douglass and Norton<sup>13</sup> using identical conditions for either the disulfide or thiol as the starting material but varying the amount of acetic anhydride to accommodate the stoichiometry. Melting points were taken on a Mel-Temp apparatus and are uncorrected.

TABLE III  
Ir and nmr spectroscopic data for substituted 2-hydroxydiaryl sulfoxides



Entry #	Ir (cm <sup>-1</sup> ) <sup>a</sup>		Nmr chemical shift <sup>b,c</sup> in ppm (coupling constants in Hz in parentheses) of observed groups <sup>d</sup>							
	OH	S = O	OH	3	4	5	6	2'	3'	4'
1	3060	1017	9.45	6.77(9)		CH <sub>3</sub> = 2.25				
2	3055	1008	9.92	6.80(9.2)		CH <sub>2</sub> = 2.57(7.5) CH <sub>3</sub> = 1.17(7.5)				
3	3150	1013	9.82	6.79(9.0)		CH = 2.84(7.0) (CH <sub>3</sub> ) <sub>2</sub> = 1.17(7.0)				
4	3170	1020	9.32	6.80(8.0, 1.0)		(CH <sub>3</sub> ) <sub>3</sub> = 1.27				
5	3050	995	9.8	6.83(9.5)		(CH <sub>3</sub> ) <sub>2</sub> = 1.22 CH <sub>2</sub> = 1.56(7.0) CH <sub>3</sub> = 0.62(7.0)				
6	3060	1010 995	9.47	6.82(9)		(CH <sub>3</sub> ) <sub>2</sub> = 1.32 CH <sub>2</sub> = 1.67 (CH <sub>3</sub> ) <sub>3</sub> = 0.65				
7	3210	1010	— <sup>c</sup>	6.96(9.0)		C <sub>6</sub> H <sub>5</sub> =				
8	3120	1005 995	9.89	CH <sub>3</sub> = 2.14	6.90	CH <sub>3</sub> = 2.22	6.98			
9	3060	1010 998	9.5	CH <sub>3</sub> = 2.18	7.09(3)	(CH <sub>3</sub> ) <sub>3</sub> = 1.27	7.24(3)			
10	— <sup>c</sup>	990	9.85	(CH <sub>3</sub> ) <sub>3</sub> = 1.33	6.88(2)	CH <sub>3</sub> = 2.25	7.15(2)			
11	3050	985	10.42	(CH <sub>3</sub> ) <sub>3</sub> = 1.37	7.09(2.3)	(CH <sub>3</sub> ) <sub>3</sub> = 1.28				
12 <sup>e</sup>	3050	1020 1005 995	10.1	6.67	CH <sub>3</sub> = 2.14	CH <sub>3</sub> = 2.14				
13 <sup>f</sup>	— <sup>c</sup>	990	10.83	6.51	CH <sub>3</sub> = 2.23	6.56	CH <sub>3</sub> = 2.29			
14 <sup>e</sup>	3110	992	10.20	6.77(8.5)	7.12(8.5, 2.5)	CH <sub>3</sub> = 2.24	7.47(2.5)	7.60(8.5)	7.27(8.5)	CH <sub>3</sub> = 2.30
15	3030	990	9.85	6.78(9)		CH <sub>2</sub> = 2.55(7.5) CH <sub>3</sub> = 1.15(7.5) CH = 2.82(6.5) (CH <sub>3</sub> ) <sub>2</sub> = 1.17(6.5)		7.57(8.5)		CH <sub>3</sub> = 2.32
16	3040	1000	9.66	6.79(9)		(CH <sub>3</sub> ) <sub>3</sub> = 1.25				CH <sub>3</sub> = 2.32
17	3010	990	9.59	6.80(9.5)		(CH <sub>3</sub> ) <sub>2</sub> = 1.22		7.59(8.3)		CH <sub>3</sub> = 2.34
18	3060	996	9.63	6.72(9)		CH <sub>2</sub> = 1.57(7.5) CH <sub>3</sub> = 0.64(7.5) (CH <sub>3</sub> ) <sub>2</sub> = 1.31 CH <sub>2</sub> = 1.67 (CH <sub>3</sub> ) <sub>3</sub> = 0.64		7.55(8)		CH <sub>3</sub> = 2.34
19	3010	985	9.57	6.80(8)				7.56(8.5)	7.24(8.5)	CH <sub>3</sub> = 2.34
20 <sup>e</sup>	3140	1005	— <sup>c</sup>	6.98(8.5)		C <sub>6</sub> H <sub>5</sub> =	7.97(2.5)			CH <sub>3</sub> = 2.30
21	3170	1021 1010	9.95	CH <sub>3</sub> = 2.18	7.05(2.2)	(CH <sub>3</sub> ) <sub>3</sub> = 1.25	7.23(2.2)	7.56(8.5)	7.24(8.5)	CH <sub>3</sub> = 2.32
22	3020	990	10.5	(CH <sub>3</sub> ) <sub>3</sub> = 1.34	6.85(2)	CH <sub>3</sub> = 2.24	7.11(2)	7.59(8.5)	7.24(8.5)	CH <sub>3</sub> = 2.33
23	— <sup>c</sup>	992	10.3	(CH <sub>3</sub> ) <sub>3</sub> = 1.37	7.05(2.5)	(CH <sub>3</sub> ) <sub>3</sub> = 1.27	7.35(2.5)	7.55(8)	7.23(8)	CH <sub>3</sub> = 2.34
24	3110	1025 1010	10.07	6.78(9)		CH <sub>3</sub> = 2.23		7.65(9)	7.44(9)	(CH <sub>3</sub> ) <sub>3</sub> = 1.28
25	3030	1003	9.67	6.95(9)		C <sub>6</sub> H <sub>5</sub> =				(CH <sub>3</sub> ) <sub>3</sub> = 1.27
26	3200— 2950	991	10.27	CH <sub>3</sub> = 2.18		(CH <sub>3</sub> ) <sub>3</sub> = 1.27				(CH <sub>3</sub> ) <sub>3</sub> = 1.28
27 <sup>e</sup>	3080	1020	10.38	6.92(8)	7.15(8.2)	CH <sub>3</sub> = 2.28	7.49(2)	7.55(9)	7.78(9)	Cl

<sup>a</sup> The infrared spectra were obtained as KBr pellets, unless otherwise indicated.

<sup>b</sup> The nmr spectra were obtained on deuteriochloroform solutions unless otherwise indicated. Chemical shifts are reported downfield from internal TMS.

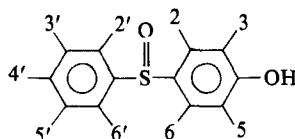
<sup>c</sup> Where no value is reported, either no value could be assigned or none was observed.

<sup>d</sup> Where the identification of the group is not indicated in the nmr data, the group is a proton.

<sup>e</sup> The nmr spectrum was obtained on DMSO-d<sub>6</sub> solutions.

<sup>f</sup> The ir spectrum was obtained on a neat film of the material.

TABLE IV  
Ir and nmr spectroscopic data for substituted 4-hydroxydiaryl sulfoxides



Entry #	Ir <sup>a</sup> (cm <sup>-1</sup> )		Nmr chemical shift <sup>b</sup> in ppm (coupling constants in Hz in parentheses) of observed groups <sup>c</sup>				
	OH	S = O	OH	2,6	3,5	2',6',3',5'	4'
1 <sup>d</sup>	3125	997	10.07	CH <sub>3</sub> = 2.35	6.59		
		986					
2 <sup>d</sup>	3050	1005	10.2	7.54(9)	6.92(9)		
		993					
3 <sup>e</sup>	3460	1015	5.67	7.43	(CH <sub>3</sub> ) <sub>3</sub> = 1.38		
4 <sup>e</sup>	3070	1003	9.42	7.43(9)	6.92(9)	7.47 (singlet)	(CH <sub>3</sub> ) <sub>3</sub> = 1.28
5 <sup>d</sup>	3080	1001	10.26	7.58(9)	6.96(9)	7.75, 7.72 (singlets)	Cl

<sup>a</sup> The infrared spectra were obtained as KBr pellets.

<sup>b</sup> Chemical shifts are reported downfield from internal TMS.

<sup>c</sup> Where the identification of the group is not indicated in the nmr data, the group is a proton.

<sup>d</sup> The solvent for the nmr solutions was DMSO-d<sub>6</sub>.

<sup>e</sup> The solvent for the nmr solutions was deuteriochloroform.

Elemental analyses were performed at the B. F. Goodrich Avon Lake Technical Center or Research and Development Center at Brecksville and at Huffman Laboratories, Inc., Wheatridge, Colorado.

#### GENERAL PROCEDURE FOR THE PREPARATION OF HYDROXYDIARYL SULFOXIDES

The arenesulfinyl chloride (one equivalent) in methylene chloride is added dropwise to a well-stirred suspension or solution of the phenol (one equivalent) and anhydrous aluminum chloride (one equivalent) in methylene chloride at 0–5°C under a nitrogen atmosphere. This mixture is stirred at 0–5°C for about 3 hours. Water is added slowly until all the resulting solid is dissolved. The organic layer is separated, dried (anhydrous MgSO<sub>4</sub>), filtered, and evaporated to afford a solid or dark oil, which slowly (or partially) solidifies. This material can be purified by washing with cold solvent or by recrystallization.

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