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Methyl Sulfinates as Electrophiles in Friedel−Crafts Reactions. Synthesis of Aryl Sulfoxides

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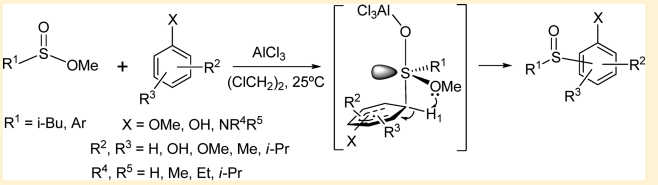
Supporting Information

ABSTRACT: The Friedel−Crafts reaction of methyl alkyl- and arylsulfinates with aromatic systems, activated by one or more electron-donating substituents (OH, OMe, NHR, NR_2), provides alkyl aryl and diaryl sulfoxides under mild conditions and in moderate to good yields. The very high regioselectivity usually observed in these sulfinylation reactions is rationalized on the basis of a Wheland intermediate having a trigonal bypyramidal structure in which steric and electronic interactions are significant factors strongly destabilizing the attack to the ortho positions.



INTRODUCTION

The great importance of the sulfoxides in organic synthesis justifies the large efforts made in the search for efficient methods for their preparation.[1] The oxidation of thioethers[2] and the reaction of organometallic compounds with sulfinic acid derivatives are among the most used methods for the preparation of sulfoxides (mainly in enantiomerically pure form),[3] but other methods involving the reaction of sulfinyl carbanions with electrophiles and rearrangements of sulfenic acid esters have also been reported.[1]

The Friedel−Crafts sulfinylation of aromatic compounds to form diaryl or alkyl aryl sulfoxides is relatively unexplored given that the synthesis of phenyl *p*-tolyl sulfoxide from benzene and *p*-toluenesulfinyl chloride was reported in 1926.[4] More than 30 years later, Douglas et al.[5] reported a 26% yield of methyl phenyl sulfoxide by reaction of benzene with methanesulfinyl chloride in the presence of anhydrous aluminum chloride, and Replogle and Maynard[6] described low yields of the corresponding sulfoxides for the direct electrophilic sulfinylation of the azulene ring with alkane or arenesulfinyl chlorides. Olah and Nishimura[7] have reported the high selectivity of the aluminum chloride catalyzed arenesulfinylation of benzene and polymethylbenzenes with substituted benzenesulfinyl chlorides in nitromethane solution, whereas Chasar and Pratt[8] prepared a number of 2- and 4-hydroxydiaryl sulfoxides by the direct arenesulfinylation of substituted phenols in the presence of anhydrous aluminum chloride.

All of the above methods are related by the use of alkyl or arylsulfinyl chlorides to induce the electrophilic aromatic substitution under Lewis acid catalysis. A problem associated with these procedures (probably responsible for their low use for obtaining sulfoxides) is the usually moderated stability of the sulfinyl chlorides (they are easily hydrolyzed), determining its easy decomposition in air and imposing the need of their use freshly prepared. In this sense, the use as electrophiles of alkyl sulfinates, much more stable and therefore easier to store and handle, could be a good alternative if they were reactive enough under Friedel−Crafts conditions. However, a pioneer report from Olah and Nishimura[9] indicated that most of the sulfinates (*i*-propyl, *t*-butyl, benzyl, *p*-methoxybenzyl, *m*-methoxybenzyl, and *p*-methylbenzyl arenesulfinates) gave alkylation instead of sulfinylation of benzene and toluene in nitromethane solution using aluminum chloride as a catalyst, which could explain that there is not any other further reference centered in the study of sulfinates as sulfinylating electrophiles in Friedel−Crafts reactions. However, in ref 9, the low reactivity of the *p*-nitrobenzyl and ethyl arenesulfinates (they only reacted in the presence of neat aluminum chloride) and the unreactivity of methyl benzenesulfinate are also reported. The low stability of the *p*-nitrobenzyl and ethyl carbenium ions, and the even lower stability of the CH_3^+ (resulting from methyl sulfinates), can explain this behavior. This result suggested to us that methyl sulfinates would be the only appropriate sulfinylating agents under Friedel−Crafts conditions. The failure to generate sulfoxides in the reactions studied in ref 9 suggests that the aromatic systems used as substrates (benzene and toluene) were too unreactive to be sulfinylated by methyl sulfinates.

We have recently reported the advantages of using methyl sulfinates instead of sulfonyl chlorides for obtaining sulfonamides.[10] The notable differences in reactivity with oxygenated nucleophiles

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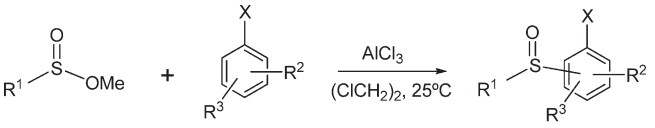
Scheme 1. Synthesis of Sulfoxides from Methyl Arenesulfinates via Friedel–Crafts Reactions



R^1 = Alkyl, Aryl X = OMe, OH, NR^4R^5
R^2, R^3 = H, OH, OMe, Me, *i*-Pr
R^4, R^5 = H, Me, Et, *i*-Pr

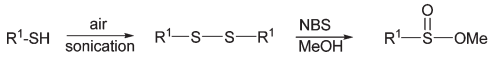
determines a much higher stability of the sulfinates, whereas both are similarly reactive with nitrogen-based nucleophiles. On this basis, we reasoned that methyl sulfinates might also exhibit a good reactivity with carbon-based nucleophiles like those involved in the Friedel–Crafts reactions, thus providing a new entry for synthesizing diaryl and alkyl aryl sulfoxides from stable and easily available substrates. The low reactivity of toluene and benzene with methyl sulfinates under conditions used in ref 9 indicated that any study concerning the use of these substrates in Friedel–Crafts reactions should consider more activated aromatic systems, such as phenols or anilines. In this paper, we describe the results obtained in these reactions (Scheme 1) with the aim of revealing their main features (reactivity, regioselectivity, and possible mechanism) as well as the scope of methyl sulfinates as sulfinylating reagents.

RESULTS AND DISCUSSION

The methyl sulfinates used in this study (**1**) were easily synthesized by a two-step process from the commercially available thiols by simple oxidation to the disulfides with air under sonication,[11] which were directly transformed into the methyl sulfinates by the method of Brownbridge et al.[12] (Scheme 2).

We first studied the reactions of methyl benzenesulfinate **1a** (1 equiv) with anisole (2 equiv) in the presence of $AlCl_3$ (1 equiv). After 15 h at rt, we observed the exclusive formation of the 4-(phenylsulfinyl)anisole **2a** in 53% isolated yield (entry 1, Table 1). This result demonstrated that methyl sulfinates could be successfully used as electrophiles in the sulfinylation of an activated aromatic system. The complete regioselectivity of this reaction suggested significant differences with respect to conventional Friedel–Crafts reactions of methoxylated aromatic substrates. Friedel–Crafts sulfinylation reactions are much more sensitive to the steric and/or electronic repulsions between reagent and the OMe group, determining that it exclusively orientates the electrophile to its *para* position. The fact that 4-methylanisole does not react after 48 h under similar conditions (entry 2) agrees with the exclusive *para* orientating character of the OMe group in these reactions, which would also explain the complete regioselective transformation of 3-methylanisole and 2-methylanisole into the sulfoxides **3a** (entry 3) and **4a** (entry 4), respectively, resulting in the attack of the sulfinate to the *para* position of the OMe group. Unexpectedly, reactivity of 3-methylanisole is lower than that of the anisole (compare reaction times and yields of entries 1 and 3), but it could be explained by assuming that steric repulsion exerted by the Me group on its *ortho* positions must be more marked than the activation produced by its electronic effects. However, the fact that 2-methylanisole exhibits an even lower reactivity (**4a** is obtained in 20% yield after six days, entry 4) is not easily understandable, and it could be suggesting that the

Scheme 2. Synthesis of Methyl Sulfinates from Thiols



1a (R^1 = Ph)
1b (R^1 = p-Tol)
1c (R^1 = p-Cl-C_6H_4)
1d (R^1 = *i*-Bu)

methyl group decreases the activating character of the *o*-OMe group as a consequence of partial steric inhibition of the resonance.

Phenol is also activated enough to react with methyl benzenesulfinate. However, it yields a mixture of *ortho* and *para* derivatives with *para* substitution being favored by a factor of 4 (entry 5). The smaller size of the OH group as compared to the methoxy moiety, and mainly its ability to form hydrogen bonds with the electrophile, thus partially compensating for their stereoelectronic repulsion, must be responsible for the formation of the *ortho* product (absent in reaction from anisole, entry 1). As expected, the *para*:*ortho* selectivity decreases when the reaction was performed at 80 °C (entry 5), but the yield remains almost unaltered. The incorporation of a methyl group into the phenol ring causes significant changes in the regioselectivity. As expected, *p*-cresol gave **7a** exclusively (entry 6). *m*-Cresol (entry 7) afforded a 90:10 mixture of compounds **8a** and **9a**, where the incorporation of the electrophile at C-6 (*ortho* with respect to the OH group) predominates over the attack at C-4 (*para* to the OH group). This inversion of the regioselectivity, with respect to that observed for phenol (entry 5), is presumably due to the steric hindrance exerted by the methyl group at C-2 and C-4. A comparison of entries 3 (exclusive attack to C-4) and 7 (predominant attack at C-6) confirms that the OMe group only orients *para*, whereas the OH allows the incorporation of the sulfinyl group at the *ortho* and *para* positions. The behavior of *o*-cresol (entry 8) is the expected one, with a regioselectivity similar to that of phenol (compare entries 5 and 8). The incorporation of the methyl group *ortho* to the hydroxyl group does not have a significant effect on the reactivity.

The introduction of a methoxy group into phenol also produces interesting changes in the regioselectivity. The behavior of the monomethyl derivative of the hydroquinone (entry 9) is the expected one (only sulfoxide **12a**, resulting from attack of the sulfinate at C-2, is formed). 3-Methoxyphenol yields a mixture of **13a** and **14a** (entry 10) with the attack at C-6 (*ortho* with respect to the OH group), predominating over attack at C-4 (*para* to the hydroxyl group). This behavior is understandable taking into account the previously commented difficulties of the sulfinate for approaching to the *ortho* positions of the OMe group. Reaction of guaiacol is completely regioselective, affording only the sulfoxide **15a**, derived from attack at C-4 (entry 11), despite that it is deactivated by the OMe group at C-2. These facts can be explained by the existence of an intramolecular hydrogen bond between the phenolic OH and the *ortho*-OMe group, which confers a higher deactivating character to the positively charged OMe group (thus decreasing the reactivity) and reduces the intermolecular association of the OH with the electrophile.

The results obtained in the sulfinylation of naphthols and their *O*-methyl derivatives (entries 12–15) deserve special comment. β-Oxygenated naphtalene is sulfinylated only in the α-position, which is specially activated by the other ring (entries 12 and 13). The higher reactivity of the β-naphthol with respect to its *O*-methyl derivative (shorter reaction times and better yields) is easily explained on the basis of the negative effect exerted by

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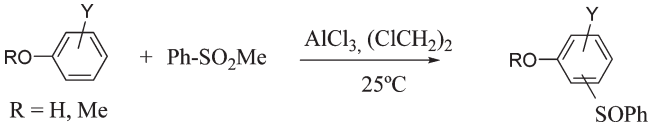
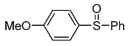
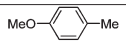
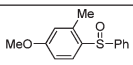
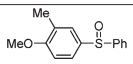
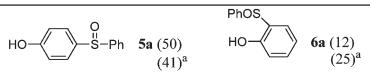
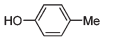
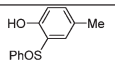
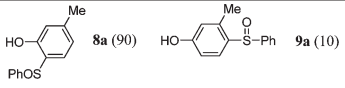
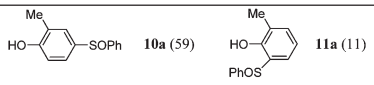
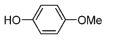
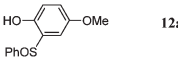
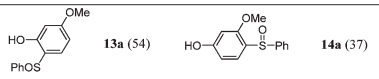
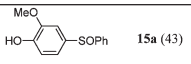
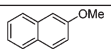
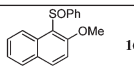
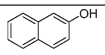
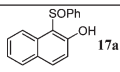
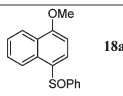
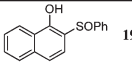
Table 1. Reactions of Aromatic Methyl Ethers, Phenols, and Napthols with Methyl Benzenesulfinate



Entry	Starting Material	Products (% Isolated Yield)	Reaction Time (h)
1		 **2a** (53)	15
2		No reaction	48
3		 **3a** (20)	36
4		 **4a** (20)	144
5		 **5a** (50) (41)[a] **6a** (12) (25)[a]	15
6		 **7a** (50)	22
7		 **8a** (90) **9a** (10)	24
8		 **10a** (59) **11a** (11)	24
9		 **12a** (63)	48
10		 **13a** (54) **14a** (37)	22
11		 **15a** (43)	48
12		 **16a** (65)	48
13		 **17a** (75)	24
14		 **18a** (67)	48
15		 **19a** (42)	48

[a] T = 80 °C.

the OMe group on the attack at its *ortho* positions (see before). It also explains the exclusive formation of the 4-sulfinyl derivative **18a** from 1-methoxynaphthalene (entry 14), as well as its higher reactivity with respect to that of 2-methoxynaphthalene (compare reaction times and yields in entries 12 and 14). However, the reaction time required for 1-methoxynaphthalene is higher than that observed for anisole (compare entries 1 and 14), which suggests that attack at C-4 of 1-methoxynaphthalene is less facile than expected for electronic reasons. The sulfinylation of 1-naphthol occurs exclusively at C-2 to give **19a** (entry 15). This behavior was not expected taking into account the reaction of phenol (entry 5) which affords a mixture of regioisomers where the *p*-sulfinyl derivative is predominant. It also indicates some factor making difficult the attack to C-4 of 1-naphthol, indicating that the *ortho* orientating character of the OH group is much higher for 1-naphthol than for phenol.

In Table 2 are collected some results obtained in the sulfinylation of other activated phenols with methyl sulfinates at room temperature. All of them give a single product in very high yields. We have also examined the reactivity of several substituted methyl arenesulfinates (Ar = Ph, *p*-Tol, and *p*-Cl-C_6H_4) with several of these phenol derivatives, and only one product was

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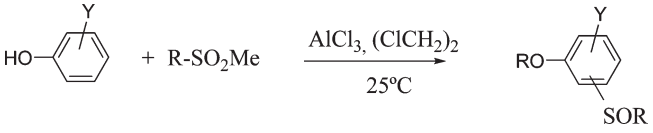
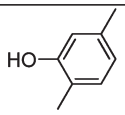
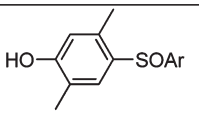
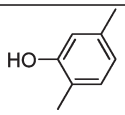
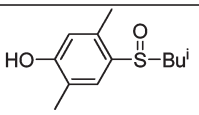
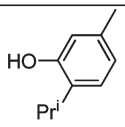
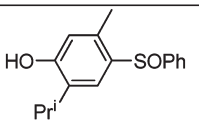
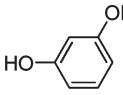
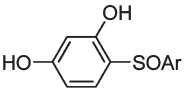
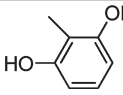
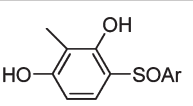
Table 2. Reactions of Different Phenols with Methyl Sulfinates



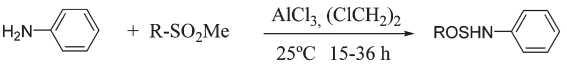
Entry	Starting Material	Products (% Isolated Yield)	Reaction Time (h)
1		 **20a** (Ar =Ph, 89%) **20b** (Ar=Tol, 50%) **20c** (Ar=*p*-Cl-C_6H_4, 80%)	22 36 24
2		 **20d** (22%)	36
3		 **21a** (75%)	15
4		 **22a** (Ar=Ph, 98%) **22b** (Ar=Tol, 97%) **22c** (Ar=*p*-Cl-C_6H_4, 80%)	22 24 24
5		 **23a** (Ar=Ph, 84%) **23b** (Ar=Tol, 93%) **23c** (Ar=*p*-Cl-C_6H_4, 83%)	8 24 24

observed in every case (compare entries 1, 4, and 5 in Table 2). We have also studied the reaction of methyl isobutylsulfinate with 2,5-dimethylphenol (entry 2). The lower yield obtained under conditions similar to those used with arenesulfinates is not unexpected due to the inductive effect of the alkyl group and agrees with their expected lower reactivity.

We then studied the sulfinylation of the anilines and derivatives. Despite that the aromatic rings of these compounds will be more activated than those of the phenols, suggesting they will be able to react with methyl sulfinates under similar conditions, the reactions of aniline with methyl phenyl sulfinate and various *p*-substituted derivatives thereof gave sulfinamides exclusively and efficiently (Scheme 3). This means that the nucleophilic power of the nitrogen is much higher than that of the aromatic carbons. Interestingly, the time required for completing the attack of nitrogen to sulfur is 15−36 h, similar to those of the phenols in Table 2 to afford aryl sulfoxides. The lower nucleophilicity of the phenolic oxygen suggests it would require longer times to form the sulfinates, which supports that these are not intermediates in the formation of the sulfoxides (see later), which must be therefore formed by direct Friedel−Crafts reactions of the phenols.

Next, we studied the behavior of *N*-alkyl and *N*,*N*-dialkylanilines (Table 3). The reaction with the N,N-disubstituted anilines

Scheme 3. Reactions of Aniline with Methyl Sulfinates



(**24a**) R=Ph (93%)
(**24b**) R=Tol (84%)
(**24c**) R=p-Cl-C_6H_4 (80%)
(**24d**) R=i-Bu (82%)

gave compounds **25**−**27** exclusively (entries 1−3, Table 3) with sulfinylation occurring only *para* to the nitrogen atom. This can also be explained by assuming a large stereoelectronic hindrance of the NR_2 at the *ortho* positions, resulting in the exclusive attack at the *para* position. This is not unexpected given that it had been also observed with anisoles (Table 1) and that the size of the NR_2 group is considerably larger than that of the OMe group. The only notable fact is the lower yield usually observed as the size of the N-substituents is increased (*i*-Pr < Et < Me), which could be a consequence of the loss of conjugation (steric inhibition of the resonance of the lone electron pair at nitrogen with the ring) produced to minimize the steric interaction of the R group with the *ortho* hydrogens. Reaction of *N*,*N*-dimethylaniline with alkyl sulfinates like methyl isobutylsulfinate

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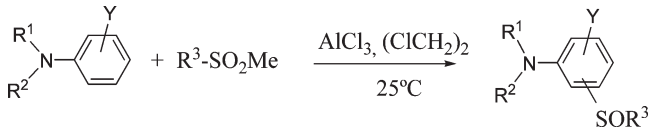
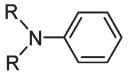
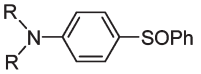
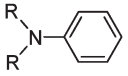
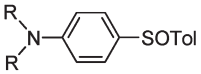
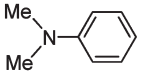
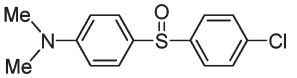
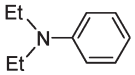
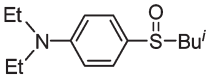
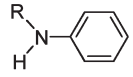
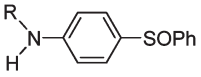
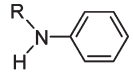
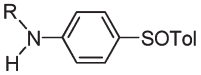
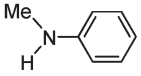
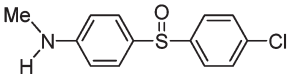
Table 3. Reactions of *N*-Alkyl and *N,N*-Dialkylanilines with Methyl Arenesulfinates



Entry	Starting Material	Products (% Isolated Yield)	Reaction Time (h)
1	 R=Me, Et, *i*-Pr	 **25a** (R=Me, 75%) **26a** (R=Et, 67%) **27a** (R=*i*-Pr, 47%)	22
2	 R=Me, Et, *i*-Pr	 **25b** (R=Me, 68%) **26b** (R=Et, 52%) **27b** (R=*i*-Pr, 23%)	36
3		 **25c** (57%)	24
4		 **26d** (63%)	36
5	 R=Me, Et, *i*-Pr	 **28a** (R=Me, 68%) **29a** (R=Et, 52%) **30a** (R=i-Pr, 43%)	15 26 24
6	 R=Me, *i*-Pr	 **28b** (R=Me, 53%) **30b** (R=*i*-Pr, 29%)	24 24
7		 **28c** (66%)	24

exhibits a similar behavior only yielding compound **26d** in good yield (entry 4, Table 3).

The sulfinylation of mono-*N*-alkylanilines are also occurs exclusively in the *para* position yielding compounds **28**−**30** (entries 5−7). As in the case of the N,N-disubstituted congeners, the yields decrease as the size of the alkyl group increases. It is worth noting the difference in the orientating power of the NHMe (only *p*-sulfinyl derivatives are obtained) and the OH groups (yielding *ortho*/*para* mixtures), which could be due to the lower ability of the NH group to form hydrogen bonds and to the larger size of the NHMe group.

To explain the observed regiochemistry of these processes, we propose that reactions of methyl sulfinates with aromatic rings containing OMe and NR_2 groups are Friedel−Crafts type sulfinylation processes, catalyzed by $AlCl_3$, where the tetrahedral sulfur is attacked by the ring carbons with higher aromatic density. The sulfur in the Wheland intermediate **A** has a trigonal bipyramid structure with the aromatic carbon and the oxygen joined to sulfinyl sulfur occupying the apical positions. The equatorial positions are occupied by the lone electron pair, the R group (aliphatic or aromatic), and the methoxy moiety (Figure 1). To minimize the steric interactions of these equatorial substituents with the aromatic ring acting as a nucleophile, the lone electron pair is arranged toward the ring (it is also favored by its electrostatic attraction with the positively charged ring), which determines that H(1) bisects the two larger equatorial substituents. The Wheland intermediate **A** evolves into **B** transferring the hydrogen (probably to the OMe group thus increasing its ability as a leaving group) and regenerating the aromatic system. Elimination of methanol from **B** (this process will presumably require a pseudorotation placing the OMe group at the apical position) would yield the final sulfoxide. This general mechanism will be followed by amines and ethers when the attacked position lacks substituents at the *ortho* sites. If one or both of these positions is occupied by a substituent (in this paper, Me, OMe, NR_2), reactions are much more difficult because of the steric and/or electronic repulsions between the *ortho* substituent and the equatorial substituent on the sulfur (**A** or **A′** in Figure 1). This would explain the exclusive *para* orientating character of the OMe and NR_2 groups. The attack at C-1 and C-4 (α positions)

dx.doi.org/10.1021/jo2006335 |*J. Org. Chem.* 2011, 76, 4635–4644

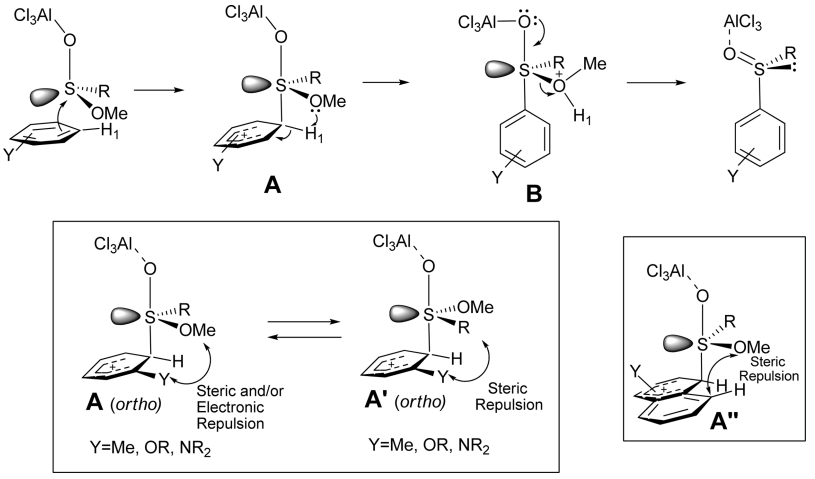
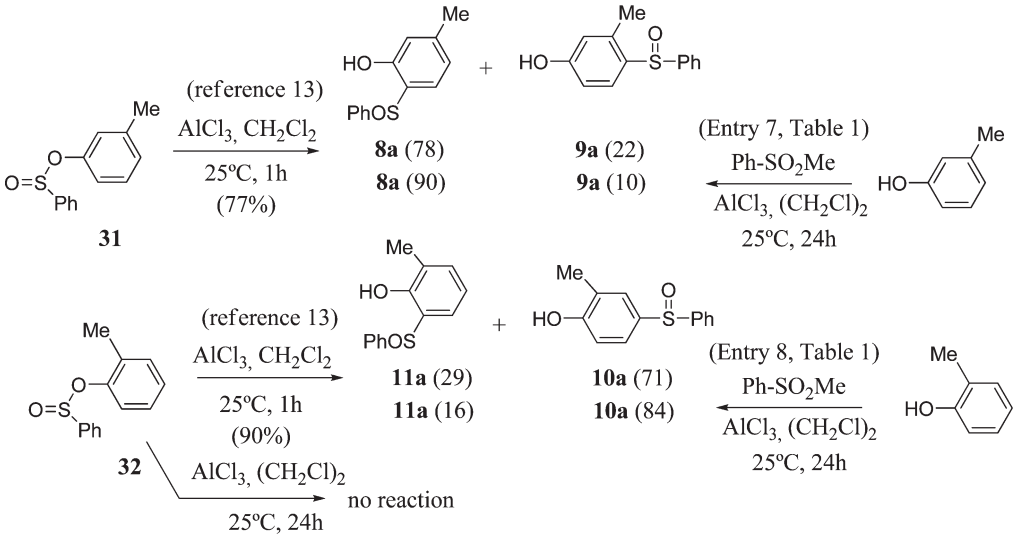


Figure 1. Mechanistic proposal for explaining the Friedel–Crafts sulfinylation reactions with methyl sulfinates.

Scheme 4. Comparison of the Results Obtained in Sulfinylation of Phenols and Rearrangement of Aryl Benzenesulfinates



of the naphthalene rings must be relatively destabilized by the steric interaction of the equatorial sulfur substituents and C-8 and C-5, respectively (**A**″ in Figure 1), determining that it was less favored than expected from electronic reasons.

Phenols show a behavior different from anisoles. The OH group mainly orientates to the *para* position, but it is able to form the *ortho* sulfinyl derivatives, which was not possible for the OMe compounds. There are two possible explanations for this difference. The first one involves assuming a different mechanism for both substrates. Since the Thia–Fries rearrangement of the aryl benzenesulfinates to *ortho* and *para* sulfinyl phenols catalyzed by Lewis acids has been reported,[13] we could assume that reactions of phenols with methyl sulfinates yield aryl sulfinates in a first step, which will be further transformed into the corresponding sulfoxides. To check this proposal, the results obtained when some aryl sulfinates are exposed to reaction conditions similar or identical to those used in Table 1 are indicated in Scheme 4. Jung et al.[13] reported the reactions of **31** and **32** with $AlCl_3$ (2 equiv) in CH_2Cl_2 at room temperature in 1 h. The results indicate that the reactivity, yield, and mainly regioselectivity are different from those shown in entries 7 and 8 of Table 1 (Scheme 4). It suggests that **31** and **32** do not act as the intermediates in reactions from *m*-cresol and *o*-cresol. However, it could be argued that the conditions are not exactly the same, because Jung used 2 equiv of $AlCl_3$ in CH_2Cl_2, whereas only 1 equiv of the catalyst in $(CH_2Cl)_2$ was used for the results shown in Table 1. Thus, we performed the reaction of **32** under the same conditions used in entry 8 in Table 1 (Scheme 4), and we recovered the starting benzenesulfinates, which unequivocally demonstrates that they cannot be intermediates in the conditions we have used for the sulfinylation of phenols.[14]

The second explanation for understanding the different behavior of phenols and anisoles consists of assuming that the attack of the methyl sulfinates at the *ortho* position of phenols is favored by the formation of hydrogen bonds between the OH and the sulfinate oxygen atoms. This would minimize the stereoelectronic repulsion between the oxygenated functions shown in Figure 1, making the formation of the *ortho* sulfinyl derivatives easier (A^1, Figure 2). The exclusive formation of the *p*-tolylsulfinyl derivatives starting from guaiacol (entry 11,

dx.doi.org/10.1021/jo2006335 |*J. Org. Chem.* 2011, 76, 4635–4644

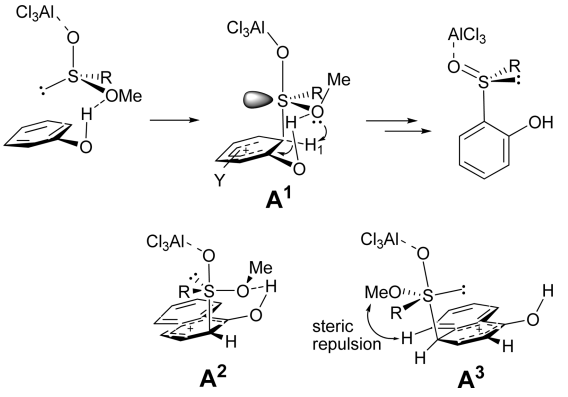


Figure 2. Mechanistic proposal for explaining the Friedel–Crafts sulfinylation of phenols and naphthols.

Table 1), where the intramolecular association of the OMe group with the OH group reduces the likelihood of forming an intermolecular hydrogen bond with the sulfinate oxygens, agrees with this explanation. On the other hand, the exclusive 2-sulfinylation of 1-naphthol (entry 15, Table 1) is understandable if we take into account that A^3, the intermediate resulting in the attack at the *para* position, must be less stable than A^2 due to the 1,3-*syn* diaxial interactions of the OMe group with the second ring (Figure 2). Moreover, the fact that 1-naphthol is more acidic than phenol suggests stronger hydrogen bonds in the first case, which would also favor the attack at the *ortho* position of 1-naphthol.

In conclusion, we report in this paper that methyl sulfinates can be used as electrophiles in Friedel–Crafts reactions with aromatic systems activated by OH, OR, NHR, and NR_2 groups under $AlCl_3$ catalysis, providing a new entry for the synthesis of aryl sulfoxides under mild conditions which avoid the use of the unstable and hazardous sulfinyl chlorides. The orientating character of the substituents is different from that shown in other S_EAr reactions, with the steric interactions seriously restricting the approach of the methyl sulfinates to their *ortho* positions, unless substituents and electrophiles can be associated by a hydrogen bond. This is a consequence of the trigonal bipyramidal structure around the sulfur adopted by the Wheland intermediate of these reactions.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out in anhydrous 1, 2-dichloroethane under argon and monitored by TLC on silica gel. Flash chromatography was performed on silica gel 60 (230–400 mesh ASTM). Melting points were determined in open capillary tubes and are uncorrected. The IR spectra were recorded with an FT-IR spectrophotometer. The ^1H and ^{13}C NMR spectra were acquired at 200 (or 300) and 50.3 (or 75.5) MHz, respectively. Mass spectra were obtained with a double sector mass spectrometer. Compounds **2a**,[15] **5a**,[8,16] **6a**,[16] **7a**,[8] **16a**,[17] **17a**,[17,18] **24a**,[19,20] **24b**,[20] **24c**,[20] **25a**,[21] **25b**,[21] and **25c**[22] have been previously described in the literature.

General Procedure for the Synthesis of Sulfoxides and Sulfinamides. To a stirred suspension of aluminum chloride (0.5 mmol) in 0.3 mL of 1,2-dichloroethane was added a solution of methyl sulfinate **1** (0.5 mmol) in 0.3 mL of 1,2-dichloroethane. The mixture was stirred at room temperature for 1 h. Then a solution of the corresponding starting material (1 mmol) in 0.3 mL of 1,2-dichloroethane was added, and the resulting mixture was stirred for the time indicated in Tables 1–3 and in the text. After the addition of CH_2Cl_2 (10 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na_2SO_4), and concentrated. The residue was purified as indicated for each case below.

4-Methoxy-2-methyl-1-(phenylsulfinyl)benzene (3a). The product was purified by flash chromatography (hexane–EtOAc, 6:4), brown oil. IR (KBr): 1599, 1479, 1442, 1287, 1242, 1041 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.81 (s, 3H), 6.70 (d, J = 2.4 Hz, 1H), 6.88 (dd, J = 2.7, 8.7 Hz, 1H), 7.40–7.49 (m, 3H), 7.53–7.60 (m, 2H), 7.75 (d, J = 8.7, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.7, 55.3, 112.4, 116.5, 125.4, 127.5, 129.1, 130.7, 134.3, 138.3, 145.1, 161.8. EIMS: m/z 246 (100%, M^+), 229 (52), 227 (42), 198 (38), 168 (51), 137 (63), 108 (33). HRMS-FAB: m/z [M^+] calcd for $C_{14}H_{14}O_2S$, 246.0715; found, 246.0718.

4-Methoxy-3-methyl-1-(phenylsulfinyl)benzene (4a). The product was purified by flash chromatography (hexane–EtOAc, 6:4), yellow oil. IR (film): 1592, 1492, 1443, 1254, 1088, 1043 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.20 (s, 3H), 3.84 (s, 3H), 6.86 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 1.5 Hz, 1H), 7.41–7.51 (m, 4H), 7.59–7.63 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.3, 55.5, 110.1, 124.6, 125.0, 127.4, 129.1, 130.6, 136.0, 136.5, 145.9, 160.3. EIMS: m/z 246 (45%, M^+), 198 (100), 183 (26), 169 (62), 153 (35), 137 (80), 77 (12). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{14}H_{15}O_2S$, 247.0793; found, 247.0799.

5-Methyl-2-(phenylsulfinyl)phenol (8a). The product was purified by flash chromatography (hexane–EtOAc, 8:2), mp 160–162 °C. IR (KBr): 2988 (br), 1602, 1562, 1302, 1233, 987 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 2.34 (s, 3H), 6.67 (d, J = 2.1 Hz, 1H), 6.82 (dd, J = 2.4, 8.4 Hz, 1H), 7.40–7.46 (m, 3H), 7.52–7.60 (m, 3H), 9.30 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 18.4, 114.3, 117.8, 125.2, 127.7, 128.9, 130.4, 132.1, 138.5, 144.9, 160.1. EIMS: m/z 232 (15%, M^+), 183 (23), 109 (100), 77 (14). HRMS-FAB: m/z [M^+] calcd for $C_{13}H_{12}O_2S$, 232.0558; found, 232.0556.

3-Methyl-4-(phenylsulfinyl)phenol (9a). The product was purified by flash chromatography (hexane–EtOAc, 7:3), mp 163–165 °C. IR (KBr): 3063 (br), 1595, 1414, 1009 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H), 6.70 (s, 1H), 6.72 (d, J = 7.5 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.46–7.50 (m, 3H), 7.65–7.70 (m, 2H), 10.02 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 120.0, 120.9, 124.7, 125.9, 129.4, 130.0, 131.3, 144.0, 144.2, 159.3. EIMS: m/z 232 (95%, M^+), 184 (100), 110 (33), 77 (28). HRMS-FAB: m/z [M^+] calcd for $C_{13}H_{12}O_2S$, 232.0558; found, 232.0556.

2-Methyl-4-(phenylsulfinyl)phenol (10a). The product was purified by flash chromatography (hexane–EtOAc, 5:5), mp 160–162 °C. IR (deposited film): 3146 (br), 1589, 1497, 1408, 1280, 1084, 1012 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 2.19 (s, 3H), 6.90 (d, J = 8.1 Hz, 1H), 7.29 (dd, J = 2.1, 8.1 Hz, 1H), 7.33 (d, J = 1.8 Hz, 1H), 7.40–7.49 (m, 3H), 7.56–7.62 (m, 2H) (the OH proton was not observed). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 16.0, 115.4, 124.5, 124.9, 126.3, 128.1, 128.9, 130.3, 134.1, 145.5, 158.6. EIMS: m/z 232 (45%, M^+), 216 (15), 184 (100), 155 (47), 139 (18), 123 (31), 110 (57), 94 (28), 77 (22). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{13}H_{13}O_2S$, 233.0636; found, 233.0635.

2-Methyl-6-(phenylsulfinyl)phenol (11a). The product was purified by flash chromatography (hexane–EtOAc, 8:2), mp 80–82 °C. IR (film): 3160 (br), 1582, 1464, 1430, 1255, 1079 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 3H), 6.82 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.43–7.60 (m, 3H), 7.63–7.73 (m, 2H), 10.36 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.3, 119.3, 122.1, 123.7, 124.7, 128.9, 129.5, 131.3, 134.2, 143.6, 157.6. EIMS: m/z 232 (100%, M^+), 216 (14), 200 (10), 184 (34), 110 (24), 77 (15). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{13}H_{13}O_2S$, 233.0636; found, 233.0634.

4-Methoxy-2-(phenylsulfinyl)phenol (12a). The product was purified by flash chromatography (hexane–EtOAc, 7:3), brownish solid, mp 143–145 °C. IR (KBr): 3166 (br), 1503, 1420, 1254, 1194, 1048, 1019 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.75 (s, 3H), 6.76

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(d, J = 2.7 Hz, 1H), 6.82 (d, J = 9.0 Hz, 1H), 6.91 (dd, J = 2.7, 9.0 Hz, 1H), 7.46−7.56 (m, 3H), 7.67−7.75 (m, 2H), 9.70 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.9, 110.3, 119.3, 120.3, 123.3, 124.9, 129.5, 131.5, 143.5, 152.8 (2C). EIMS: m/z 248 (100%, M^+), 231 (51), 216 (16), 200 (34). HRMS-FAB: m/z [M^+] calcd for $C_{13}H_{12}O_3S$, 248.0507; found, 248.0510.

5-Methoxy-2-(phenylsulfinyl)phenol (13a). The product was purified by flash chromatography (hexane−EtOAc, 7:3), mp 141−142 °C. IR (KBr): 3062, 1594, 1421, 1277, 1210, 1004 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 3.76 (s, 3H), 6.41 (d, J = 2.4 Hz, 1H), 6.50 (dd, J = 2.4, 8.7 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 7.41−7.49 (m, 3H), 7.65−7.70 (m, 2H), 10.09 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 54.8, 102.3, 106.0, 118.1, 124.2, 126.2, 128.5, 130.2, 144.6, 158.0, 162.9. EIMS: m/z 248 (53%, M^+), 232 (6), 200 (100), 171 (47). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{13}H_{13}O_3S$, 249.0585; found, 249.0593.

3-Methoxy-4-(phenylsulfinyl)phenol (14a). The product was purified by flash chromatography (hexane−EtOAc, 7:3), mp 121−126 °C. IR (KBr): 3106, 1582, 1429, 1206, 1006 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.62 (s, 3H), 6.39 (d, J = 1.8 Hz, 1H), 6.55 (dd, J = 1.8, 8.7 Hz, 1H), 7.39−7.46 (m, 4H), 7.59−7.65 (m, 2H), 8.63 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6, 99.7, 109.0, 121.1, 125.2, 127.4, 129.0, 130.8, 144.2, 158.2, 162.3. EIMS: m/z 248 (21%, M^+), 232 (13), 231 (46), 200 (100), 171 (23). HRMS-FAB: m/z [M + 1]$^+$ calcd for $C_{13}H_{13}O_3S$, 249.0585; found, 249.0582.

2-Methoxy-4-(phenylsulfinyl)phenol (15a). The product was purified by flash chromatography (hexane−EtOAc, 35:65), brownish oil. IR (KBr): 3182 (br), 1584, 1504, 1444, 1417, 1272, 1085, 1030 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.87 (s, 3H), 6.96 (d, J = 8.1 Hz, 1H), 7.13 (dd, J = 2.1, 8.1 Hz, 1H), 7.18 (d, J = 2.1 Hz, 1H), 7.42−7.49 (m, 3H), 7.58−7.63 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.1, 106.9, 114.8, 119.7, 124.6, 129.2, 130.8, 136.1, 145.7, 147.6, 148.7. EIMS: m/z 248 (54%, M^+), 200 (100), 185 (23), 171 (64), 139 (63), 110 (41). HRMS-FAB: m/z [M^+] calcd for $C_{13}H_{12}O_3S$, 248.0507; found, 248.0505.

1-Methoxy-4-(phenylsulfinyl)naphthalene (18a). It was obtained following the general procedure slightly modified as follows: 1.0 mmol of methyl sulfinate and 0.5 mmol of 1-methoxynaphthalene were used. The product was purified by flash chromatography (hexane−EtOAc, 2:1), brownish oil. IR (film): 1620, 1572, 1508, 1460, 1380, 1322, 1271, 1245, 1089, 1044 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.02 (s, 3H), 6.92 (d, J = 8.2 Hz, 1H), 7.34−7.41 (m, 3H), 7.45−7.54 (m, 2H), 7.62−7.66 (m, 2H), 8.07 (d, J = 8.2 Hz, 1H), 8.19−8.24 (m, 1H), 8.27−8.33 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8, 103.3, 122.5, 123.0, 125.1, 125.9, 126.0, 126.5, 127.8, 129.1, 130.5, 131.1, 145.4, 158.5. MS (FAB+): m/z 283 (100%, M+H$^+$). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{17}H_{15}O_2S$, 283.0793; found, 283.0784.

2-(Phenylsulfinyl)naphthalen-1-ol (19a). It was obtained following the general procedure. The 1-naphthol was added undissolved in 1,2-dichloroethane. The product was purified by flash chromatography (hexane−diethyl ether, 5:1), brown solid, mp 81−83 °C. IR (film): 3057 (br), 1627, 1574, 1444, 1397, 1300, 1080 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 8.6 Hz, 1H), 7.44−7.58 (m, 5H), 7.73−7.77 (m, 3H), 8.29 (app d, J = 7.7 Hz, 1H), 11.5 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.5, 119.6, 121.2, 122.4, 125.0, 126.0, 126.3, 127.5, 128.5, 129.5, 131.6, 135.4, 143.9, 157.1. MS (FAB+): m/z 269 (100%, M + H$^+$), 268 (46%, M^+), 251 (38). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{16}H_{13}O_2S$, 269.0636; found, 269.0641.

2,5-Dimethyl-4-(phenylsulfinyl)phenol (20a). The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 154−156 °C. IR (KBr): 3092, 1399, 1265, 1004 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 3H), 2.30 (s, 3H), 6.65 (s, 1H), 7.40−7.47 (m, 4H), 7.52−7.57 (m, 2H), 9.20 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.4, 17.8, 116.7, 123.6, 124.8, 127.8, 128.7, 130.1, 131.3, 135.3, 145.0, 158.0. EIMS: m/z 246 (100%, M^+), 229 (66), 198 (23), 168 (51), 137 (33), 110 (28), 77 (26). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{14}H_{15}O_2S$, 247.0793; found, 247.0797.

2,5-Dimethyl-4-(*p*-tolylsulfinyl)phenol (20b). The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 165−167 °C. IR (KBr): 3116, 1402, 1267, 1023 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.14 (s, 3H), 2.23 (s, 3H), 2.37 (s, 3H), 6.55 (s, 1H), 7.24−7.42 (AA′BB′system, 4H), 7.41 (s, 1H), 7.82 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.6, 18.1, 21.4, 117.4, 123.9, 125.5, 128.4, 129.9, 131.7, 136.0, 140.8, 141.3, 157.7. EI MS: m/z 260 (100%, M^+), 243 (69), 241 (54), 212 (34), 168 (98), 124 (40), 108 (36), 91 (25). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{15}H_{17}O_2S$, 261.0949; found, 261.0956.

4-(4-Chlorophenylsulfinyl)-2,5-dimethylphenol (20c). The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 170−173 °C. IR (KBr): 3081, 1609, 1391, 1258, 986 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$ + DMSO-d_6): δ 2.18 (s, 3H), 2.31 (s, 3H), 6.64 (s, 1H), 7.37−7.51 (m, 5H) (the OH proton was not observed). ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ 15.6, 18.1, 117.1, 124.2, 126.6, 128.3, 129.2, 131.4, 135.8, 136.5, 143.8, 158.4. EIMS: m/z 280 (7%, M^+), 214 (24), 200 (28), 183 (36), 165 (31), 91 (100). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{14}H_{14}ClO_2S$, 281.0403; found, 281.0403.

4-(Isobutylsulfinyl)-2,5-dimethylphenol (20d). The product was purified by flash chromatography (hexane−EtOAc, 8:2), yellow oil. IR (KBr): 3132, 2959, 1268, 998 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.06 (d, J = 6.6 Hz, 3H), 1.14 (d, J = 6.6 Hz, 3H), 2.23 (s, 3H), 2.25 (s, 3H), 2.20−2.30 (m, 1H), 2.47 (dd, J = 9.2, 13.0 Hz, 1H), 2.83 (dd, J = 4.8, 13.0 Hz, 1H), 6.64 (s, 1H), 7.58 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.6, 17.8, 21.6, 22.8, 24.3, 65.9, 116.9, 124.2, 126.4, 131.1, 134.1, 157.5. EIMS: m/z 226 (30%, M^+), 170 (100), 122 (65), 107 (32). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{12}H_{19}O_2S$, 227.1106; found, 227.1098.

2-Isopropyl-5-methyl-4-(phenylsulfinyl)phenol (21a). The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 144−145 °C. IR (KBr): 3112, 2961, 1408, 1256, 1012 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13 (d, J = 6.9 Hz, 3H), 1.14 (d, J = 6.9 Hz, 3H), 2.20 (s, 3H), 3.18 (sp, J = 6.9 Hz, 1H), 6.60 (s, 1H), 7.40−7.46 (m, 3H), 7.50−7.56 (m, 3H), 7.91 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.0, 22.2, 22.3, 27.0, 117.9, 124.7, 125.6, 129.1, 130.7, 131.4, 134.4, 135.8, 144.2, 157.2. EIMS: m/z 274 (100%, M^+), 257 (42), 226 (10), 215 (56), 196 (53), 165 (42), 110 (78). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{16}H_{19}O_2S$, 275.1106; found, 275.1107.

4-(Phenylsulfinyl)benzene-1,3-diol (22a). The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 125−127 °C. IR (deposited film): 3250, 3043, 1591, 1442, 1234, 1170 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 6.38 (d, J = 2.4 Hz, 1H), 6.44 (dd, J = 2.4, 8.4 Hz, 1H), 7.43 (m, 3H), 7.65 (m, 2H), 9.45 (br s, 1H), 9.86 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 104.2, 107.8, 116.1, 124.3, 126.7, 128.6, 130.1, 144.7, 158.4, 161.5. EIMS: m/z 234 (67%, M^+), 218 (9), 186 (100), 157 (32). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{12}H_{11}O_3S$, 235.0429; found, 235.0428.

4-(*p*-Tolylsulfinyl)benzene-1,3-diol (22b). The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 75−78 °C. IR (KBr): 3159 (br), 1593, 1458, 1247, 1176 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 2.37 (s, 3H), 6.38 (d, J = 2.4 Hz, 1H), 6.42 (dd, J = 2.4, 8.4 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 7.25−7.52 (AA′BB′system, 4H), 9.10 (s, 1H), 10.13 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 21.2, 105.6, 108.1, 114.4, 124.8, 127.4, 129.9, 141.4 (2C), 160.4, 161.9. EIMS: m/z 248 (59%, M^+), 232 (28), 200 (100), 91 (18). HRMS-FAB: m/z [$M + 1$]$^+$ calcd for $C_{13}H_{13}O_3S$, 249.0585; found, 249.0583.

4-(4-Chlorophenylsulfinyl)benzene-1,3-diol (22c). The product was purified by flash chromatography (hexane−EtOAc, 6:4), colorless oil. IR (film): 3163 (br), 1593, 1471, 1176 cm^{-1}. ^{1}H NMR

(200 MHz, $CDCl_3$ + DMSO-d_6): δ 6.39 (d, J = 2.4 Hz, 1H), 6.45 (dd, J = 2.4, 8.4 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 7.42−7.57 (AA′BB′system, 4H), 9.18 (br s, 1H), 9.86 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ 105.4, 108.4, 114.7, 126.1, 127.4, 129.4, 137.0, 143.0, 159.9, 162.2. EIMS: m/z 268 (45%, M^+), 252 (58), 220 (100), 157 (50), 112 (34). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{12}H_{10}ClO_3S$, 269.0030; found, 269.0030.

2-Methyl-4-(phenylsulfinyl)benzene-1,3-diol (23a). The product was purified by flash chromatography (hexane−EtOAc, 7:3), mp 128−129 °C. IR (deposited film): 3150, 2923, 1593, 1304, 1179 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H), 6.48 (d, J = 8.5 Hz, 1H), 6.98 (d, J = 8.5 Hz, 1H), 7.45 (m, 3H), 7.60 (m, 2H), 8.87 (br s, 1H), 10.12 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 7.5, 107.2, 113.2, 114.4, 124.2, 124.5, 129.1, 130.7, 144.1, 158.5, 159.9. EIMS: m/z 248 (84%, M^+), 232 (26), 200 (100), 171 (43). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{13}H_{13}O_3S$, 249.0585; found, 249.0587.

2-Methyl-4-(*p*-tolylsulfinyl)benzene-1,3-diol (23b). The product was purified by flash chromatography (hexane−EtOAc, 7:3), mp 160−163 °C (dec). IR (KBr): 3321, 1604, 1430, 1081 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 2.03 (s, 3H), 2.37 (s, 3H), 6.46 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 7.26−7.49 (AA′BB′system, 4H), 8.87 (s, 1H), 10.26 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 7.5, 21.1, 107.1, 113.3, 114.4, 124.0, 124.6, 129.8, 141.2 (2C), 158.6, 159.7. EIMS: m/z 262 (70%, M^+), 246 (15), 214 (100), 91 (12). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{14}H_{15}O_3S$, 263.0742; found, 263.0747.

4-(4-Chlorophenylsulfinyl)-2-methylbenzene-1,3-diol (23c). The product was purified by flash chromatography (hexane−EtOAc, 8:2), yellow oil. IR (film): 3191, 1600, 1472, 1308, 1080 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.05 (s, 3H), 5.99 (br s, 1H), 6.43 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 7.44−7.54 (AA′BB′system, 4H), 10.08 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 7.4, 107.2, 114.0, 114.4, 124.5, 126.0, 129.6, 137.4, 142.2 (2C), 158.7. EIMS: m/z 282 (58%, M^+), 266 (29), 234 (100), 171 (47), 83 (21). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{13}H_{12}ClO_3S$, 283.0196; found, 283.0196.

2-Methyl-*N*-phenylpropane-1-sulfinamide (24d). It was obtained following the general procedure with 36 h of reaction time. The product was purified by flash chromatography (hexane−EtOAc, 8:2), mp 52−54 °C. IR (KBr): 3417, 3158, 2961, 1600, 1495, 1041 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.03 (d, J = 6.8 Hz, 3H), 1.09 (d, J = 6.8 Hz, 3H), 2.15 (m, 1H), 2.83 (dd, J = 8.0, 12.8 Hz, 1H), 2.94 (dd, J = 6.4, 13.0 Hz, 1H), 6.96−7.08 (m, 3H), 7.19−7.29 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.8, 22.3, 24.6, 64.7, 118.3, 123.0, 129.4, 141.3. EIMS: m/z 197 (42%, M^+), 141 (60), 140 (68), 93 (100), 92 (67), 57 (52). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{10}H_{16}NOS$, 198.0953; found, 198.0945.

***N,N*-Diethyl-4-(phenylsulfinyl)aniline (26a).** The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 161−164 °C. IR (deposited film): 3058, 2972, 1591, 1509, 1272, 1097 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.14 (t, J = 7.1 Hz, 6H), 3.36 (q, J = 7.1 Hz, 4H), 6.60−6.66 (half of an A_2X_2 system, 2H), 7.38−7.47 (m, 5H), 7.58−7.63 (half of an A_2X_2 system, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.4, 44.4, 111.3, 124.6, 128.2, 128.9, 129.6, 130.1, 146.1, 150.1. EIMS: m/z 273 (71%, M^+), 258 (35), 225 (59), 210 (74), 196 (100), 181 (50), 133 (28). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{16}H_{20}NOS$, 274.1266; found, 274.1258.

***N,N*-Diethyl-4-(*p*-tolylsulfinyl)aniline (26b).** The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 80−83 °C. IR (KBr): 2968, 1589, 1509, 1089, 1039 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.14 (t, J = 7.0 Hz, 6H), 2.37 (s, 3H), 3.35 (q, J = 7.0 Hz, 4H), 6.62 (half of an A_2X_2 system, 2H), 7.24−7.50 (AA′BB′system, 4H), 7.41 (half of an A_2X_2 system, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 12.3, 21.3, 44.4, 111.2, 124.6, 128.0, 129.6 (2C), 140.4, 142.9, 149.9. EIMS: m/z 287 (72%, M^+), 272 (30), 239 (68), 224 (100), 196 (91), 181 (33). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{17}H_{22}NOS$, 288.1422; found, 288.1427.

***N,N*-Diethyl-4-(isobutylsulfinyl)aniline (26d).** The product was purified by flash chromatography (hexane−EtOAc, 8:2), colorless oil. IR (film): 3214, 2996, 1594, 1510, 1093, 1032 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (d, J = 6.6 Hz, 3H), 1.10 (d, J = 6.6 Hz, 3H), 1.18 (t, J = 7.2 Hz, 6H), 2.05−2.20 (m, 1H), 2.45 (dd, J = 8.4, 12.9 Hz, 1H), 2.88 (dd, J = 5.4, 12.9 Hz, 1H), 3.39 (q, J = 7.2 Hz, 4H), 6.72 (half of an A_2X_2 system, 2H), 7.47 (half of an A_2X_2 system, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.3, 21.8, 22.7, 24.2, 44.4, 66.9, 111.3, 126.4, 127.8, 149.9. EIMS: m/z 253 (8%, M^+), 222 (16), 196 (100), 181 (44), 152 (12). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{14}H_{24}NOS$, 254.1579; found, 254.1573.

***N,N*-Diisopropyl-4-(phenylsulfinyl)aniline (27a).** The product was purified by flash chromatography (hexane−EtOAc, 8:2), mp 109−112 °C. IR (KBr): 2967, 1589, 1508, 1293, 1034 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (d, J = 6.9 Hz, 6H), 1.26 (d, J = 6.9 Hz, 6H), 3.87 (sp, J = 6.9 Hz, 1H), 6.77−6.83 (half of an A_2X_2 system, 2H), 7.36−7.48 (m, 5H), 7.59−7.64 (half of an A_2X_2 system, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 21.1, 47.4, 115.4, 124.6, 127.4, 128.9, 130.1, 130.4, 146.0, 150.7. EIMS: m/z 301 (52%, M^+), 286 (100), 244 (75), 119 (28). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{18}H_{24}NOS$, 302.1579; found, 302.1570.

***N,N*-Diisopropyl-4-(*p*-tolylsulfinyl)aniline (27b).** The product was purified by flash chromatography (hexane−EtOAc, 7:3), mp 95−97 °C. IR (KBr): 2972, 1589, 1505, 1292, 1039 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.25 (d, J = 6.8 Hz, 6H), 1.26 (d, J = 7.0 Hz, 6H), 2.37 (s, 3H), 3.87 (sp, J = 6.8 Hz, 2H), 6.79 (half of an A_2X_2 system, 2H), 7.25−7.51 (AA′BB′ system, 4H), 7.38 (half of an A_2X_2 system, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 21.0, 21.3, 47.3, 115.3, 124.6, 127.2, 129.6, 130.5, 140.5, 142.7, 150.6. EIMS: m/z 315 (38%, M^+), 300 (100), 258 (61), 119 (23). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{19}H_{26}NOS$, 316.1735; found, 316.1728.

***N*-Methyl-4-(phenylsulfinyl)aniline (28a).** The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 121−122 °C. IR (KBr): 3339, 1600, 1526, 1087, 1020 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.83 (s, 3H), 4.09 (br s, 1H), 6.57 (half of an A_2X_2 system, 2H), 7.38−7.48 (m, 5H), 7.59 (half of an A_2X_2 system, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.2, 112.3, 124.6, 127.9, 128.9, 130.2, 131.9, 146.2, 151.9. EIMS: m/z 231 (35%, M^+), 215 (9), 183 (100), 154 (89), 122 (37). HRMS-FAB: m/z $[M^+]$ calcd for $C_{13}H_{13}NOS$, 231.0718; found, 231.0719.

***N*-Methyl-4-(*p*-tolylsulfinyl)aniline (28b).** The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 148−150 °C (dec). IR (KBr): 3324, 1607, 1088, 1010 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.82 (s, 3H), 4.18 (br s, 1H), 6.57 (half of an A_2X_2 system, 2H), 7.24−7.47 (AA′BB′ system, 4H), 7.41 (half of an A_2X_2 system, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.3, 30.2, 112.2, 124.6, 127.8, 129.6, 131.9, 140.6, 142.9, 151.8. EIMS: m/z 245 (25%, M^+), 197 (100), 154 (52), 122 (27).

4-(4-Chlorophenylsulfinyl)-*N*-methylaniline (28c). The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 145−147 °C (dec). IR (KBr): 3312, 1607, 1086, 1015 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.84 (s, 3H), 4.22 (br s, 1H), 6.57 (half of an A_2X_2 system, 2H), 7.38−7.42 (AA′BB′system, 4H), 7.52 (half of an A_2X_2 system, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 30.1, 112.2, 125.9, 128.0, 129.2, 131.2, 136.4, 144.7, 152.1. EIMS: m/z 265 (30%, M^+), 217 (100), 154 (95), 122 (31). HRMS-FAB: m/z $[M^+]$ calcd for $C_{13}H_{13}ClNOS$, 266.0406; found, 266.0403.

***N*-Ethyl-4-(phenylsulfinyl)aniline (29a).** The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 80−82 °C. IR (KBr): 3304, 1598, 1524, 1086, 1025 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (t, J = 7.1 Hz, 3H), 3.14 (q, J = 7.1 Hz, 2H), 6.56 (half of an A_2X_2 system, 2H), 7.36−7.47 (m, 5H), 7.59 (half of an A_2X_2 system,

2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.5, 37.9, 112.4, 124.6, 128.0, 128.9, 130.2, 131.6, 146.0, 151.0. EIMS: m/z 245 (54%, M^+), 229 (8), 197 (88), 182 (54), 168 (100), 153 (28), 136 (29). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{14}H_{16}NOS$, 246.0953; found, 246.0947.

***N*-Isopropyl-4-(phenylsulfinyl)aniline (30a).** The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 76−78 °C. IR (deposited film): 3314, 1597, 1522, 1089, 1029 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (d, J = 6.3 Hz, 6H), 3.61 (sp, J = 6.3 Hz, 1H), 3.95 (br s, 1H), 6.53 (half of an A_2X_2 system, 2H), 7.36−7.47 (m, 5H), 7.59 (half of an A_2X_2 system, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.7, 43.9, 112.8, 124.6, 128.1, 128.9, 130.1, 131.3, 146.1, 150.2. EIMS: m/z 259 (60%, M^+), 211 (90), 196 (81), 182 (100), 167 (18), 140 (41), 119 (23). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{15}H_{18}NOS$, 260.1109; found, 260.1103.

***N*-Isopropyl-4-(*p*-tolylsulfinyl)aniline (30b).** The product was purified by flash chromatography (hexane−EtOAc, 6:4), mp 78−80 °C. IR (KBr): 3277, 1593, 1084, 1021 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.19 (d, J = 6.2 Hz, 6H), 2.37 (s, 3H), 3.62 (sp, J = 6.2 Hz, 1H), 3.94 (br s, 1H), 6.54 (half of an A_2X_2 system, 2H), 7.24−7.48 (AA′BB′ system, 4H), 7.38 (half of an A_2X_2 system, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.3, 22.7, 43.9, 112.8, 124.6, 128.0, 129.6, 131.5, 140.6, 142.8, 150.0. EIMS: m/z 273 (50%, M^+), 225 (88), 210 (100), 182 (72), 140 (28), 119 (18), 97 (45), 83 (60). HRMS-FAB: m/z $[M + 1]^+$ calcd for $C_{16}H_{20}NOS$, 274.1266; found, 274.1263.

■ ASSOCIATED CONTENT

Supporting Information. Proton and carbon NMR spectra for all new compounds prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) In this regard, one of the referees suggested we studied the behavior of the *O*-methyl derivative of **6a** under conditions similar to those used in entry 1 of Table 1. This suggestion is based on the possibility that the *p*-substituted product **2a**, exclusively formed in the reaction of anisole, was formed by rearrangement of the kinetically formed *o*-product, thermodynamically much less stable than **2a** [in such a case, the lack of reaction of *p*-methylanisole (entry 2, Table 1) could be explained from the low thermodynamic stability of the *o*-product]. We synthesized the *O*-methyl derivative of **6a** (reaction with MeI in basic media), but it remained unaltered for 48 h under the indicated reaction conditions. It proves that 2-fenylsulfinyl anisole is not the intermediate in the formation of **2a**.

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