Graphite/Methanesulfonic Acid (GMA) as a New Reagent for Sulfonylation of Phenols and Thia-*Fries* Rearrangement of Aryl Sulfonates to Sulfonylphenols

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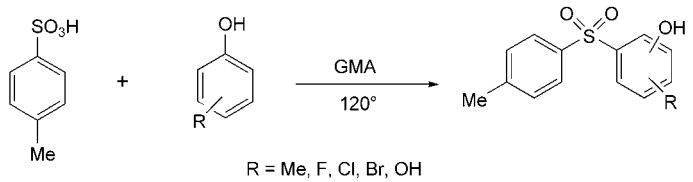
A new facile method for direct sulfonylation of phenols was developed. Graphite in methanesulfonic acid (GMA) was used to prepare sulfonylphenols by sulfonylation of phenol and naphthalene derivatives with *p*-toluenesulfonic acid (=4-methylbenzenesulfonic acid) (*Table 1*) and the thia-*Fries* rearrangement of aryl sulfonates (*Table 4*). Mechanistic studies showed that the sulfonylation reaction of phenols in GMA occurred through an initial sulfonate formation followed by a thia-*Fries* rearrangement of the aryl sulfonate by an intermolecular mechanism (*Scheme 3*).

Introduction. – Sulfones are useful intermediates in a wide range of fields such as drug and agrochemical intermediates [1], thermographic materials [2], polymers [3], antiviral agents [4], and antiseptics, and they are also useful as fungicides and bactericides [5].

The exceptional ability of graphite to adsorb organic molecules [6] and to act as a carrier of intercalated reagents is well-known [6b]. *Diels–Alder* and ene reactions [7], *Friedel–Crafts* acylations [7a], decarboxylations [7a], decompositions [8], rearrangements [7a][9], ketocarboxylations [10], oxidation of propan-2-ol [11], thermolyses of esters [12], thermal reactions in heterocyclic syntheses [13], decompositions of metal complexes [14], pyrolysis of urea [15], acylations of aromatic compounds [16], acylative cleavage of ethers [17], and conversions of aldehydes to nitriles were effected under such conditions [18]. Because graphite has a large surface area, it is a good heat conductor, and the reactions can be carried out under milder conditions [7].

We report herein that graphite in methanesulfonic acid (GMA) works as a good coupling reagent for the synthesis of sulfonylphenols from *p*-toluenesulfonic acid (=4-methylbenzenesulfonic acid) and phenols (*Scheme 1*).

Scheme 1

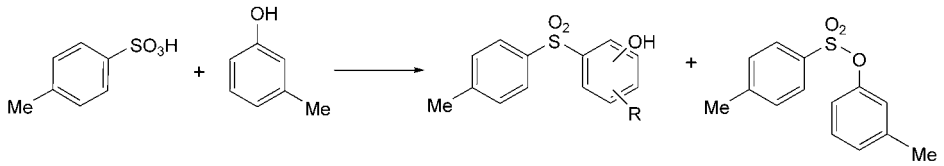


1

R = Me, F, Cl, Br, OH
GMA = graphite / $MeSO_3H$

Results and Discussion. – To exploit an effective reagent for the arylsulfonylation of phenols, the reaction of *p*-toluenesulfonic acid (**1**) with *m*-cresol (= 3-methylphenol; **2**) was chosen as a model, and its behavior was studied under a variety of conditions by TLC and ^{1}H-NMR spectroscopy (*Scheme 2*). It was found that phenol **2** was not sulfonylated with *p*-toluenesulfonyl chloride (or **1**) in the presence of $AlCl_3$ [19], $ZnCl_2$ [20], $FeCl_3$ [21], $SnCl_4$ [21], $SbCl_5$ [22], montmorillonite clay (Fe^{3+}) [21], or triflic acid (= trifluoromethanesulfonic acid) [23]. In the case of triflic acid, 3-methylphenyl 4-methylbenzenesulfonate (**4**) was obtained in 60% yield (*Scheme 2*). However, the target sulfonylphenol **3** could be prepared in 40% yield in the presence of polyphosphoric acid (PPA), while bis(4-methylphenyl) sulfone (*Jacobsen* rearrangement product [24]) was obtained as a by-product in 40% yield.

Scheme 2



1 **2** **3** **4**

The best yield (85%) of **3** was obtained from **1** and **2** in the presence of a mixture of graphite and $MeSO_3H$ (= GMA; ratio 0.3 g/1 ml), at 120° after 2 h, and this without *Jacobsen* rearrangement desulfonylation, and *trans*-sulfonation reactions (for a typical procedure, see *Exper. Part*). In the absence of $MeSO_3H$ or graphite, attempted phenylsulfonylation did not afford **3**.

To establish the generality and applicability of this GMA sulfonylation method, various phenols with both electron-donating and -withdrawing substituents were subjected to the same reaction conditions as **2** to furnish the corresponding sulfonylphenols in good yield (*Table 1*).

Activated phenols gave mixtures of two isomeric (*ortho* (*o*) and *para* (*p*)) sulfonylphenols in good yields (*Entries 1–4*). The *p*-chloro- and *p*-bromophenols selectively furnished the *o*-sulfonylphenols in 75 and 70% yields, respectively (*Entries 5* and *6*). To increase further these yields, longer reaction periods were applied but no changes in the yields occurred (see also below). It should be noted that the sulfonylation of *o*-chloro- and *o*-bromophenol gave the corresponding *p*-sulfonyl isomer selectively in 73 and 70% yield, respectively (*Entries 7* and *8*). Benzene-1,3-diol underwent the reaction to produce only the corresponding monosulfonylated product in 80% yield (*Entry 10*). However, benzene-1,4-diol did not react with **1** in the presence of GMA (*Entry 11*). In the case of the bulkier naphthalenol, the reaction was regioselective and produced essentially the 2-sulfonylated isomer (*Entry 14*). Nitro-substituted phenols did not react with **1** in the presence of GMA indicating that electrophilic substitution does not occur when an electron-withdrawing group deactivates the aromatic ring.

The relative reactivity of the aromatic substrates in the GMA sulfonylation is consistent with a mechanism involving attack at the aromatic ring by a weak electrophilic reagent that requires an electron-rich ring. Apparently, the sulfonylium

Table 1. *Sulfonylation of Phenols with* **1** *in the Presence of a Mixture of Graphite and $MeSO_3H$* (GMA) *at 120°*

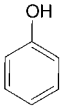
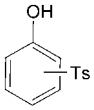
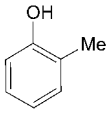
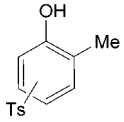
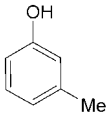
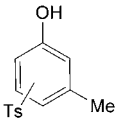
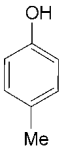
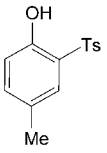
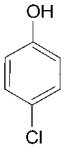
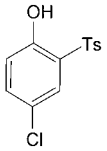
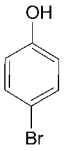
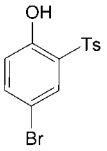
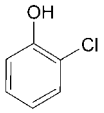
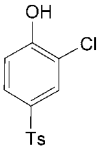
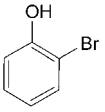
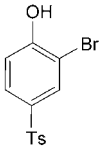
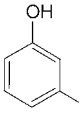
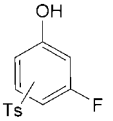
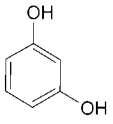
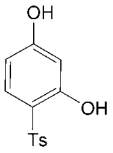
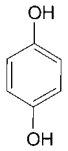
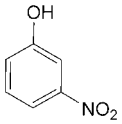
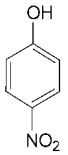
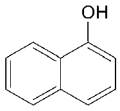
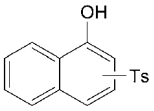
Entry	Phenols	Time [h]	Products[a])	Yield [%][b]) (*ortho*/*para*)[c])
1		2		75 (1:2)
2		2		75 (1:5)
3		2		85 (1:2)
4		2		65[d])
5		2		75
6		2		70
7		2		73
8		2		70
9		2		74 (1:1)

Table 1 (cont.)

Entry	Phenols	Time [h]	Products[a])	Yield [%][b]) (*ortho*/*para*)[c])
10		2		80
11		12	no reaction	–
12		12	no reaction	–
13		12	no reaction	–
14		2		80 (10 : 1)

[a]) Ts = tosyl = 4-$MeC_6H_4SO_2$. [b]) Isolated yield. [c]) The ratio of the products was determined by ^{1}H-NMR analysis. [d]) The *ipso* rearrangement product was also produced (13%); the product was 3-methyl-4-[(4-methylphenyl)sulfonyl]phenol.

cation, $MeC_6H_4SO_2^+$ is involved, which is very similar to the occurrence of the acyl cation $ArCO^+$ in the mechanism proposed for the formation of aromatic ketones in PPA [25].

The sulfonylation of *p*-chlorophenol (**5**) with *p*-toluensulfonic acid (**1**) in the presence of GMA (*Scheme 3*) was monitored by ^{1}H-NMR spectroscopy under different reaction conditions. The results (*Table 2*) clearly established that, in all cases, first aryl sulfonate **6** was formed, which then decomposed to give the final product **7**, the rate of its formation increasing with increasing temperature (*Scheme 3*).

The intermediacy of the aryl sulfonate was confirmed by exposing sulfonate **6** for 1 h to GMA at 120°, which gave sulfonylphenol **7** in 95% yield.

The following mechanism of the sulfonylation reaction is thus suggested: the phenol is first converted to the aryl sulfonate by reaction with *p*-toluenesulfonic acid (**1**). The aryl sulfonate subsequently undergoes rapid intermolecular decomposition in the

Scheme 3

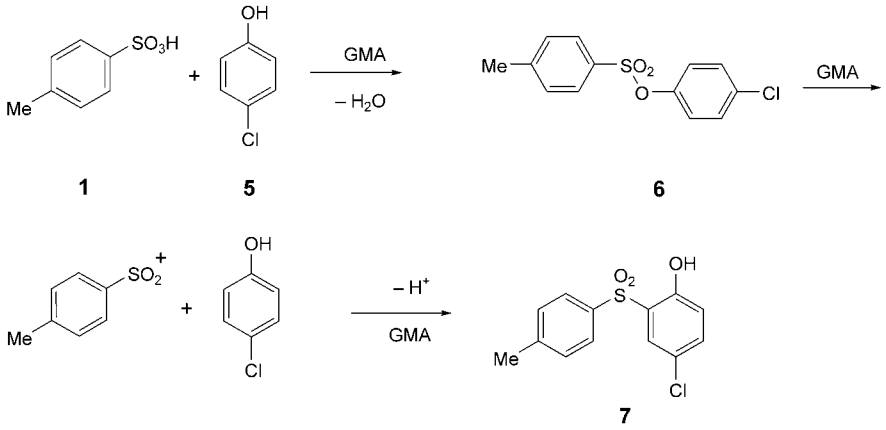


Table 2. *Sulfonylation of* p-*Chlorophenol* (**5**) *with* p-*Toluenesulfonic Acid* (**1**) *in the Presence of GMA*

Entry	Time [h]	Temp. [°]	Yield [%][a])[b])	
			6	**7**
1	8	50	–	–
2	0.5	80	–	–
3	2	80	17	–
4	4	80	35.4	–
5	8	80	40	21.7
6	12	80	32.7	42.3
7	1	100	29	–
8	2	100	36	26.4
9	4	100	34.6	42
10	0.5	120	15	–
11	1	120	12	45
12	2	120	5	75

[a]) Isolated yield. [b]) The ratio of the products was determined by ^{1}H-NMR analysis.

presence of GMA (thia-*Fries* rearrangement) to produce the sulfonylium cation $MeC_6H_4SO_2^+$ and the phenol, which combine to form the sulfonylphenols (*Scheme 3*)

To establish the intermediacy of a free sulfonylium cation in the sulfonation reaction in the presence of CMA (*Scheme 3*), the trapping of the cation by a sulfonylium acceptor should afford the same products as those obtained from the normal thia-*Fries* rearrangement. Thus, we first tested if *m*-xylene (**8**) would be an appropriate competitive acceptor by exposing it at 120° for 2 h to **1** in the presence of GMA; this was the case, since sulfonylxylene **9** was isolated in 70% yield (*Scheme 4*). We then treated a mixture of sulfonate **6** and 2.5 equiv. of *m*-xylene (**8**) with GMA at 120° (*Scheme 4*). After 1 h, no thia-*Fries* rearrangement product **7** was formed, and only compound **9** was obtained (see *Table 3*). Extending the reaction time to 4 h resulted in an equilibrium mixture containing only 14% of **7**, which was rather poor but reasonable because the aromatic ring of *p*-chlorophenol (**5**) also is reactive such as that

Scheme 4

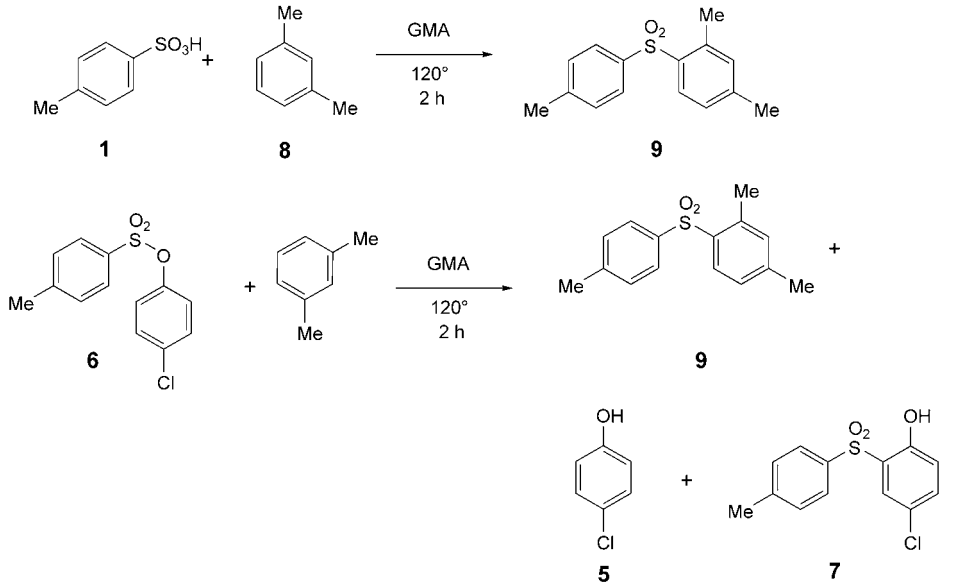


Table 3. *Progress of the Thia*-Fries *Rearrangement of Aryl Sulfonate* **6** *in the Presence of* m-*Xylene*

Time [h]	Temp. [°]	Yield [%]		
		6	**7**	**9**
0.5	120	65	–	35
1	120	55	–	45
2	120	45	5	50
3	120	30	10	60
4	120	11	14	75

of *m*-xylene (**8**). Considering these results, it can be safely concluded that the formation of sulfonylphenols by a thia-*Fries* rearrangement of the aryl sulfonate **6** occurs *via* an intermolecular mechanism.

The application of the new reagent to the thia-*Fries* rearrangement of other aryl sulfonates was also successful (see *Table 4*). Thus, GMA rearranged the aryl sulfonates to the same sulfonylphenols as those obtained in the sulfonylations of the corresponding phenols (*cf. Tables*).

In conclusion, we have demonstrated that the readily available and inexpensive reagent graphite/$MeSO_3H$ (GMA) is very effective for the direct sulfonylation of phenol and naphthalenol derivatives with *p*-toluenesulfonic acid (**1**) and for the thia-*Fries* rearrangement of aryl sulfonates. The simple procedure and workup, the lack of solvent in the reaction step, and the high yields make this method a useful addition to the present methodologies. Hence, we believe that it will find wide application in organic synthesis as well as in industry.

We gratefully acknowledge the support of this work by the *Shiraz University Research Council*.

Table 4. *Thia*-Fries *Rearrangement of Aryl Sulfonates by Using a Mixture of Graphite and $MeSO_3H$* (GMA) *at 120°*

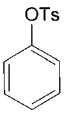
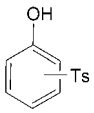
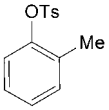
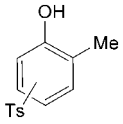
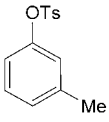
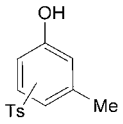
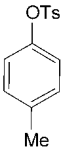
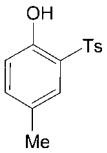
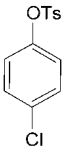
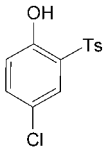
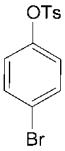
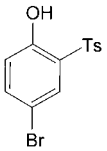
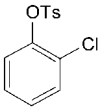
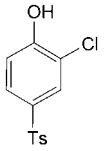
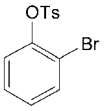
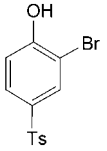
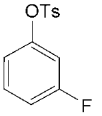
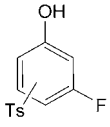
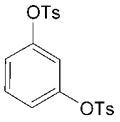
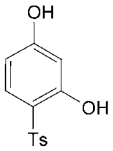
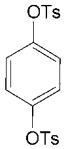
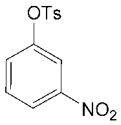
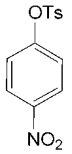
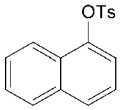
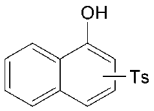
Aryl sulfonate	Time [h]	Products[a])	Yield [%][b]) (*ortho*/*para*)[c])
	1		85 (1:2)
	1		80 (1:3)
	1		90 (1:2)
	1		90[d])
	1		95
	1		90
	1		85
	1		80
	1		75 (1:1)

Table 4 (cont.)

Aryl sulfonate	Time [h]	Products[a])	Yield [%][b]) (*ortho*/*para*)[c])
	1		85
	12	no reaction	–
	12	no reaction	–
	12	no reaction	–
	1		90 (10 : 1)

[a]) Ts = tosyl = 4-Me$C_6H_4SO_2$. [b]) Isolated yield. [c]) The ratio of the products was estimated by ^{1}H-NMR analysis. [d]) The *ipso* rearrangement product was also produced (10%); the product was 3-methyl-4-[(4-methylphenyl)-sulfonyl]phenol.

Experimental Part

General. All starting materials, *p*-toluenesulfonic acid (**1**) and phenols, were used as purchased from *Fluka* or *Merck*. Graphite (flake-type; *Aldrich*) and 98% methanesulfonic acid were purchased from *Fluka*. UV Spectra: λ_{max} (ε) in nm. IR Spectra: ν in cm^{-1}. NMR Spectra: δ in ppm. MS: in *m*/*z* (rel. %).

Direct Sulfonylation of Phenols: General Procedure. To a mixture of graphite (3 g) and methanesulfonic acid (10 ml) at 120°, **1** (20 mmol) and a phenol derivative (20 mmol) were added, and the mixture was stirred for 2 h. Then the mixture was poured into H_2O, and the graphite was filtered off. The filtrate was extracted with $CHCl_3$ (2 × 25 ml), the extract washed with 5% $NaHCO_3$ soln. (2 × 20 ml), dried ($CaCl_2$), and evaporated, and the crude product purified by column chromatography (silica gel, hexane/AcOEt).

Thia-Fries *Rearrangement of Aryl Sulfonates: General Procedure.* To a mixture of graphite (3 g) and methanesulfonic acid (10 ml) at 120°, the aryl sulfonate (20 mmol) was added and stirred for 1 h. Then the mixture was poured into H_2O and worked up as described above. The synthesized sulfonylphenols are known. Specific detailed data are given below:

2-[(4-Methylphenyl)sulfonyl]phenol [26]: White crystals. M.p. 124–125° ([26]: 126°), IR (neat): 3292, 1590, 1361, 1145. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.42 (*s*, 3 H); 7.00 (*m*, 2 H); 7.30 (*d*, 2 H); 7.45 (*d*, 1 H); 7.65 (*d*, 1 H); 7.84 (*d*, 2 H); 9.26 (*s*, 1 H). MS: 248 (59.6, M^+), 172 (23.5), 94 (58.2), 65 (100).

4-[(4-Methylphenyl)sulfonyl]phenol [26]: White crystals. M.p. 143–144° ([26]: 143°). IR (neat): 3375, 1585, 1284, 1144. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.38 (*s*, 3 H); 6.30 (*s*, 1 H); 6.90 (*d*, 2 H); 7.37 (*d*, 2 H); 7.79 (*d*, 4 H). MS: 249 (100, M^+), 141 (45.8), 108 (43.4), 91 (32.6), 65 (66.2), 43 (54.7).

2-Methyl-6-[(4-methylphenyl)sulfonyl]phenol [27]: White crystals. M.p. 130–131° ([27]: 130–132°). IR (neat): 3330, 1593, 1284, 1144. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.45 (*s*, 3 H); 2.58 (*s*, 3 H); 6.80 (*t*, 1 H); 7.35 (*d*, 3 H); 7.85 (*d*, 2 H); 9.30 (*s*, 1 H). MS: 262 (100, M^+), 195 (17.6), 155 (64.6), 107 (93.0), 65 (41.3), 43 (68.5).

2-Methyl-4-[(4-methylphenyl)sulfonyl]phenol [27]: White crystals. M.p. 117–119° ([27]: 120°). IR (neat): 3367, 1590, 1283, 1147. ^{1}H-NMR ($CDCl_3$, 250 MHz) 2.25 (*s*, 3 H); 2.38(*s*, 3 H); 5.40 (*s*, 1 H); 6.80 (*d*, 1 H); 7.25 (*d*, 2 H); 7.66 (*d*, 2 H); 7.78 (*d*, 2 H). MS: 262 (0.2, M^+), 247 (98.2), 155 (11.0), 139 (100), 107 (11.1), 91 (32.7), 65 (35.9), 43 (15.1).

5-Methyl-2-[(4-methylphenyl)sulfonyl]phenol [28]: White crystals. M.p. 144-145° ([28]: 145–147°). IR (neat): 3315, 1594, 1300, 1149. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.30 (*s*, 3 H); 2.38 (*s*, 3 H); 6.65 (*s*, 1 H); 6.78 (*d*, 1 H); 7.31 (*d*, 2 H); 7.47 (*d*, 2 H); 7.77 (*d*, 2 H); 9.16 (*s*, 1 H). MS: 262 (45.4, M^+), 246 (33.4), 228 (25.7), 180 (37.9), 139 (100), 107 (21.5), 91 (91.4), 65 (83.1).

3-Methyl-4-[(4-methylphenyl)sulfonyl]phenol [28]: White crystals. M.p. 150-151° ([28] 151–152°). IR (neat): 3366, 1595, 1317, 1153. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.32 (*s*, 3 H); 2.40 (*s*, 3 H); 6.41 (*s*, 1 H); 6.65 (*s*, 1 H); 6.79 (*d*, 1 H); 7.26 (*d*, 2 H); 7.69 (*d*, 2 H); 8.04 (*d*, 1 H). MS: 262 (24.7, M^+), 244 (25.0), 227 (12.1), 196 (100), 153 (50.0), 107 (26.4), 77 (99.8).

4-Methyl-2-[(4-methylphenyl)sulfonyl]phenol [26]: White crystals. M.p. 133–134° ([26] 135°). IR (neat): 3319, 1595, 1367, 1147. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.26 (*s*, 3 H); 2.4 (*s*, 3 H); 6.9 (*d*, 1 H); 7.25 (*d*, 3 H); 7.34 (*s*, 1 H); 7.83 (*d*, 2 H); 9.08 (*s*, 1 H). MS: 262 (26.0, M^+), 186 (51.9), 107 (100), 77 (73.8), 51 (22.5).

4-Chloro-2-[(4-methylphenyl)sulfonyl]phenol [28]: White needles. M.p. 127–128° ([28]: 127°). IR (neat): 3386, 1596, 1290, 1141, 817. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.32 (*s*, 3 H); 6.68 (*d*, 1 H); 7.13 (*d*, 2 H); 7.24 (*s*, 1 H); 7.73 (*d*, 2 H); 9.10 (*s*, 1 H). MS: 282 (63.5, M^+), 215 (26.1), 126 (14.5), 108 (15.8), 92 (100), 65 (54.9), 41 (23.4).

2-Chloro-4-[(4-methylphenyl)sulfonyl]phenol [26]: White cubic crystals. M.p. 174–175° ([26]: 176°). IR (neat): 3327, 1584, 1303, 1132, 737. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.33 (*s*, 3 H); 6.07 (*s*, 1 H); 7.02 (*d*, 1 H); 7.23 (*d*, 2 H); 7.69 (*d*, 3 H); 7.85 (*s*, 1 H). MS: 282 (82.3, M^+), 175 (40.7), 139 (77.1), 108 (91.7), 9 (100), 65 (98.6), 41 (53.7).

5-Fluoro-2-[(4-methylphenyl)sulfonyl]phenol [29]: White crystals. M.p. 128–130°. IR (neat): 3345, 1591, 1279, 1148, 1090. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.35 (*s*, 3 H); 6.60 (*d*, 1 H); 7.19 (*s*, 1 H); 7.24 (*d*, 2 H); 7.58 (*t*, 1 H); 7.72 (*d*, 2 H); 9.35 (*s*, 1 H). MS: 266 (98.4, M^+), 202 (20.1), 155 (22.6), 139 (22.2), 108 (47.1), 91 (100), 65 (65.6).

3-Fluoro-4-[(4-methylphenyl)sulfonyl]phenol [29]: White crystals. M.p. 124–126°. IR (neat): 3405, 1609, 1319, 1140, 1248. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.34 (*s*, 3 H); 6.50 (*d*, 1 H); 6.68 (*s*, 1 H); 7.07 (*s*, 1 H); 7.26 (*d*, 2 H); 7.76 (*d*, 3 H). MS: 266 (44.7, M^+), 159 (26.8), 139 (37.4), 108 (65.8), 91 (57.5), 65 (50.1), 43(100).

2-[(4-Methylphenyl)sulfonyl]naphthalen-1-ol [26]: White crystals. M.p. 128–130° ([26]: 129°). IR (neat): 3150, 1570, 1120, 1350. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.37 (*s*, 3 H); 7.30 (*d*, 2 H); 7.60 (*m*, 4 H); 7.65 (*d*, 1 H); 7.85 (*d*, 2 H); 8.40 (*d*, 1 H); 10.46 (*s*, 1 H, OH). MS: 298 (91.9, M^+), 191 (19.8), 162 (10.4), 139 (57.9), 115 (50.2), 91 (42.6), 59 (47.5), 43 (100).

4-[(4-Methylphenyl)sulfonyl]-1-naphthalen-1-ol [26]: White crystals. M.p. 160° ([26]: 163°). IR (neat): 3200, 1600, 1110, 1360. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.38 (*s*, 3 H); 6.93 (*m*, 4 H); 7.26 (*d*, 2 H); 7.85 (*d*, 1 H); 7.90 (*d*, 2 H); 8.10 (*s*, 1 H); 8.21 (*d*, 1 H). MS: 298 (100, M^+); 265 (11.5), 234 (23.1), 206 (22.7), 142 (73.2), 114 (64.6), 91 (47.4), 65 (48.2), 43 (43.5).

4-[(4-Methylphenyl)sulfonyl]benzene-1,3-diol [30]: White crystals. M.p. 160–162° ([30]: 155–157°): UV ($CHCl_3$): 308.4 (1993). IR (neat): 3358, 1595, 1334, 1136. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.33 (*s*, 3 H); 5.62 (*s*, 1 H); 6.37 (*d*, 2 H); 7.20 (*d*, 2 H); 7.43 (*d*, 1 H); 7.71 (*d*, 2 H); 9.20 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 22.01; 105.02; 109.34; 126.95; 127.25; 130.42; 131.49; 132.82; 149.50; 154.32. MS: 264 (100, M^+), 199 (21.1), 157 (22.1), 125 (14.31), 108 (33.8), 91 (60.0), 65 (57.3).

4-Bromo-2-[(4-methylphenyl)sulfonyl]phenol [31]: White needles. M.p. 145–146°. UV ($CHCl_3$): 251 (2909), 307.7 (1180). IR (neat): 3388, 1469, 1290, 1141, 131. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.43 (*s*, 3 H); 6.89 (*d*, 1 H); 7.34 (*d*, 2 H); 7.51 (*d*, 1 H); 7.73 (*s*, 1 H); 7.81 (*d*, 2 H); 9.37 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 22.05; 121.12; 125.47; 125.95; 127.42; 129.81; 130.67; 134.80; 138.33; 145.83; 145.66. MS: 328 (46.9, M^+), 261 (12.2), 181 (10.5), 139 (28.0), 108 (16.4), 92 (100), 65 (58.4), 43 (47.6).

2-Bromo-4-[(4-methylphenyl)sulfonyl]phenol [31]: White crystals. M.p. 170–172°. UV ($CHCl_3$): 257.6 (2801), 301.3 (1778). IR (neat): 3327, 1593, 1299, 1110, 723. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.41 (*s*, 3 H); 6.85 (*t*, 1 H); 7.31 (*d*, 2 H); 7.64 (*d*, 2 H); 7.82 (*d*, 2 H); 9.56 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 21.96; 111.06; 117.07;

127.89; 129.38; 130.42; 132.31; 135.30; 138.93; 144.75; 156.82. MS: 326 (6.4, M^+), 155 (38.5), 108 (12.4), 91 (82.0), 69 (42.3), 43 (100).

2,4-Dimethyl-1-[(4-methylphenyl)sulfonyl]benzene (**9**) [23]: White crystals. M.p. 50° ([23]: 49°). IR (neat): 1155, 1310 (O=S=O). ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.27 (*s*, 1 Me); 2.31 (*s*, 2 Me); 6.71 (*s*, 1 H); 7.08 (*d*, 1 H); 7.14 (*d*, 2 H); 7.76 (*d*, 2 H); 8.01 (*d*, 1 H). MS: 276 (M^+), 228 (41.0), 180 (6.6), 103 (12.5), 91 (83.0), 77 (100), 51 (43.0).

Aryl Sulfonate Derivatives: General Procedure [32]. A phenol (0.05 mol) and *p*-toluenesulfonyl chloride (0.05 mol) were dissolved in acetone (50 ml) and the mixture was stirred at r.t. with a mechanical stirrer. Then 25% K_2CO_3 soln. (40 ml) was added gradually within 30 min. The sulfonate was filtered and treated with 10% aq. NaOH soln. The product was again filtered and crystallized from EtOH.

The produced aryl sulfonates are known. Specific detailed data are given below:

3-Methylphenyl 4-Methylbenzenesulfonate (**4**) [32]: White crystals. M.p. 63–64° ([321]: 62–63°). IR (neat): 1529, 1363, 1179. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.31 (*s*, 3 H); 2.46 (*s*, 3 H); 6.74 (*d*, 2 H); 6.88 (*s*, 1 H); 6.95 (*d*, 2 H); 7.04 (*d*, 1 H). MS: 262 (17.2, M^+), 155 (45.2), 91 (100), 77 (25.1), 65 (35.2), 51 (14.7).

4-Methylphenyl 4-Methylbenzenesulfonate [32]: White needles. M.p. 70–72° ([32]: 67–68°). IR (neat): 1595, 1376, 1175. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.21 (*s*, 3 H); 6.75 (*d*, 2 H); 6.97 (*d*, 2 H); 7.22 (*d*, 2 H); 7.61 (*d*, 2 H). MS: 262 (22.5, M^+), 153 (43.7), 107 (20.1), 91 (100), 77 (45.7), 65 (45.7), 51 (23.4).

2-Methylphenyl 4-Methylbenzenesufonate [32]: White crystals. M.p. 52–53° ([32]: 51°). IR (neat): 1596, 1375, 1192. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.01 (*s*, 3 H); 2.50 (*s*, 3 H); 6.78 (*d*, 1 H); 7.25 (*m*, 3 H); 7.35 (*d*, 3 H); 7.72 (*d*, 3 H). MS: 262 (18.7, M^+), 155 (43.9), 91 (100), 77 (44.7), 65 (45.7), 51 (23.4).

Phenyl 4-Methylbenzenesulfonate [32]: White crystals. M.p. 100–102° ([32]: 96–98°). IR (neat): 1595, 1382, 1176. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.47 (*s*, 3 H); 7.00 (*d*, 2 H); 7.70 (*d*, 2 H). MS: 248 (20.3, M^+), 155 (44.9), 91 (100), 65 (58.1).

4-Chlorophenyl 4-Methylbenzenesulfoate (**6**) [32]: White crystals. M.p. 78–79° ([32], 79–81°). IR (neat): 1596, 1379, 1174, 754. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.38 (*s*, 3 H); 6.82 (*d*, 2 H); 7.15 (*d*, 2 H); 7.24 (*d*, 2 H); 7.24 (*d*, 2 H); 7.95 (*d*, 2 H). MS: 282 (17.1, M^+), 155 (59.71), 91 (100), 65 (27.9).

4-Bromophenyl 4-Methylbenzenesulfonate [33]: White crystals. M.p. 92–93° ([33]: 93–95°). IR (neat): 1596, 1377, 1172 , 748. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.47 (*s*, 3 H); 6.88 (*d*, 2 H); 7.29 (*d*, 2 H); 7.41 (*d*, 2 H); 7.71 (*d*, 2 H). MS: 326 (14.6, M^+), 155 (71.3), 91 (100), 65 (29.4).

2-Chlorophenyl 4-Methylbenzenesulfonate [32]: White crystals. M.p. 81–82° ([32]: 81–83°). IR (neat): 1596, 1373,118, 765. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.55 (*s*, 3 H); 7.30 (*m*, 4 H); 7.45 (*d*, 2 H); 7.82 (*d*, 2 H). MS: 282 (23.4, M^+), 155 (87.7), 91 (100), 65 (30.8).

2-Bromophenyl 4-Methylbenzenesulfonate [33]: White crystals. M.p. 78–79° ([33]: 77–79°). IR (neat): 1595, 1301, 1176, 763. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.46 (*s*, 3 H); 7.13 (*d*, 2 H); 7.3 (*m*, 3 H); 7.51 (*d*, 2 H); 7.81 (*d*, 2 H). MS: 326 (18.0, M^+), 155 (99.6), 91 (100), 65 (28.0).

3-Fluorophenyl 4-Methylbenzenesulfonate [33]: White solid. M.p. 56–58° ([33]: 55–57°). IR (neat): 1483, 1379, 1178, 1093. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.46 (*s*, 3 H); 6.78 (*t*, 2 H); 7.00 (*d*, 1 H); 7.23 (*d*, 2 H); 7.72 (*d*, 2 H). MS: 266 (21.7, M^+), 155 (68.1), 91 (100), 65 (34.3).

Benzene-1,3-diol Bis(4-methylbenzenesulfonate) [33]: White crystals. M.p. 62–64° ([33]: 63–65°). IR (neat): 1595, 1375, 1178. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.38 (*s*, 6 H); 6.59 (*s*, 1 H); 6.85 (*d*, 2 H); 7.16 (*t*, 1 H); 7.26 (*d*, 4 H); 7.64 (*d*, 4 H). MS: 418 (10.9, M^+), 199 (14.0), 155 (65.7), 91 (100), 65 (30.5).

3-Nitrophenyl 4-Methylbenzenesulfonate [33]: White crystals. M.p. 112–114° ([33]: 114–115°). IR (neat): 1593, 13001, 1527, 1350, 1149. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.49 (*s*, 3 H); 7.28 (*d*, 2 H); 7.46 (*t*, 1 H); 7.75 (*d*, 2 H); 7.8 (*s*, 1 H); 8.14 (*d*, 1 H). MS: 293 (9.03, M^+), 155 (98.2), 91 (100), 65 (33.5).

4-Nitrophenyl 4-Methylbenzenesulfonate [33]: White crystals. M.p. 98–100° ([33]: 97°). IR (neat): 1589, 1300, 1527, 1350, 1149. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.50 (*s*, 3 H); 7.25 (*d*, 2 H); 7.35 (*d*, 2 H); 7.77 (*d*, 2 H); 8.55 (*d*, 2 H). MS: 293 (12.0, M^+), 155 (100.0), 91 (100), 65 (39.9).

Benzene-1,4-diol Bis(4-methylbenzenesulfonate) [33]: White solid. M.p. 162° ([33]: 163–164°). IR (neat): 1596, 1371, 1199. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.50 (*s*, 6 H); 6.85 (*s*, 4 H); 7.55 (*d*, 4 H); 7.75 (*d*, 4 H). MS: 418 (13.0, M^+), 155 (100), 91 (79.3), 65 (24.0).

Naphthalen-1-ol-4-Methylbenzenesulfonate [32]: White crystals. M.p. 100–101° ([32]: 99–100°). IR (neat): 1600, 1350, 1170. ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.4 (*s*, 3 H); 7.26 (*m*, 6 H); 7.42 (*d*, 2 H); 7.82 (*d*, 2 H); 7.90 (*d*, 1 H). MS: 298 (47.6, M^+), 143 (100), 115 (86.8), 91 (45.4), 65 (24.3).

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