Bismuth(III) Trifluoromethanesulfonate: An Efficient Catalyst for the Sulfonylation of Arenes

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Sulfonylation reactions are one of the most important groups of aromatic electrophilic substitutions.[1] The sulfonyl group is a widely used synthon for synthetic organic chemists,[2] and sulfones have many industrial applications.[3] In Friedel−Crafts (FC) acylation and sulfonylation, a consequence of the complexation of the Lewis acid with the reaction product implies that a stoichiometric amount of the activator is often required. However, some metal halides such as iron(III) chloride,[1] Brönsted acids, for example polyphosphoric acid[4] or triflic acid,[5] and zeolites[6,7] have been reported to catalyze the sulfonylation of arenes.

In recent years, rare earth trifluoromethanesulfonates (triflates) have been reported for the catalysis of the FC acylation[8] but not for the catalysis of the FC sulfonylation. Also, our laboratory reported that bismuth(III) chloride (**1a**) and particularly bismuth(III) triflate (**1b**) were catalysts for acylation reactions,[9] especially for FC acylation.[10] In a *stoichiometric process* from arylsulfonyl bromides, silver triflate gives trifluoromethanesulfonic arenesulfonic anhydrides ($ArSO_2OTf$), which are strong sulfonylating reagents.[11] We present here a study of the catalytic activity of **1a** and **1b** for the sulfonylation reaction of arenes (eq 1), for which **1b** proved to be a metal triflate capable of realizing an outstanding *catalytic process*.

Table 1. Sulfonylation Reactions Catalyzed by Bismuth(III) Chloride (1a)

entry	reaction[a,b]	product and isomers[c]	yield (%)[c]
1	**2** + $PhSO_2Cl$	**10** (43:7:50)[d]	22
2	**3** + $PhSO_2Cl$	**12** (32:6:62)[d]	8
3	**8** + $PhSO_2Cl$	**16**	tr
4	**2** + TsCl	**11** (45:0:55)[e]	60
5	**3** + TsCl	**18** (25:7:68)[e]	50
6	**8** + TsCl	**20**	8
7	**3** + Ts_2O	**18** (30:4:66)[e]	50

[a] See Table 2; experimental conditions: 120 °C, 5 h (entries 1,2,5−7) or 6 h (entries 3,4). [b] Catalyst: **1a** (5 mol %). [c] Determined by GC. [d,e] Various isomers: (*o*:*m*:*p*)[d], (2,4′:3,4′:4,4′)[e].

$$ArH + RSO_2X \longrightarrow ArSO_2R + HX \qquad (1)$$

Catalyst: **1a** or **1b** (1-10% mol)
$X = Cl$ or OSO_2R ; R = alkyl or aryl group

Results and Discussion

Initially, we started this study by comparing the catalytic activity of **1a** and **1b** on the sulfonylation of anisole, toluene, and chlorobenzene. Compound **1a** was a moderate catalyst for the reactions between anisole or toluene with TsCl (Table 1, entries 4,5), but its efficiency decreased strongly for those involving $PhSO_2Cl$, less reactive than TsCl (entries 1,2), or the deactivated chlorobenzene (entries 3,6). The activity of **1a** was nearly the same for the reactions of toluene with TsCl and Ts_2O (entries 5,7). For the same reactions, the catalytic activity of **1b** was much higher, in particular for the reactions involving $PhSO_2Cl$ as the reagent (Table 1, entries 1−3 and Table 2, entries 1,2,6) and those with chlorobenzene (Table 1, entries 3,8 and Table 2, entries 6,12).

Then, we extended the examples toward a series of arenes, in the presence of **1b** using an arylsulfonyl chloride as an electrophile. Compound **1b** is capable of catalyzing not only the sulfonylation of activated arenes (Table 2, entries 1−4,8,9,14,16−18) but also that of non- or weakly activated ones (entries 5,10,11). Noteworthy results were observed for the sulfonylation of deactivated chloro- and bromobenzene (entries 6,7,12,13,15). In the

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10.1021/jo9902603 CCC: $18.00

Table 2. Sulfonylation Reactions Catalyzed by Bismuth(III) Triflate (1b)

entry	reaction[a–c]	product and isomers[d]	yield (%)[e]
1	**2** + $PhSO_2Cl$	**10** (48:0:52)[g]	80
2	**3** + $PhSO_2Cl$	**12** (37:6:57)[g]	84
3	**4** + $PhSO_2Cl$	**13**[h,l]	90
4	**5** + $PhSO_2Cl$	**14**[i,l]	90
5	**6** + $PhSO_2Cl$[f]	**15**	63
6	**8** + $PhSO_2Cl$	**16** (3:0:97)[g]	70
7	**9** + $PhSO_2Cl$	**17** (2:0:98)[g]	68
8	**3** + TsCl	**18** (29:5:66)[j]	80
9	**3** + TsCl	**18** (18:3:79)[j]	70
10	**6** + TsCl[f]	**12**	65[d]
11	**7** + TsCl	**19**[k,l]	65
12	**8** + TsCl	**20**[k,l]	73
13	**9** + TsCl	**21** (2:0:98)[j]	88[d]
14	**3** + 4-F-$C_6H_4SO_2Cl$	**19** (41:7:52)[j]	80
15	**8** + 4-F-$C_6H_4SO_2Cl$	**22**[k,l]	52
16	**3** + 4-Cl-$C_6H_4SO_2Cl$	**20** (40:6:54)[j]	84
17	**3** + 4-^{t}Bu-$C_6H_4SO_2Cl$	**23** (28:4:68)[j]	90
18	**3** + 4-MeO-$C_6H_4SO_2Cl$	**11** (13:3:84)[j]	84
19	**3** + MsCl	**24** (51:12:37)[g]	53
20	**3** + ^{n}BuSO$_2$Cl	**25** (45:8:47)[g]	70
21	**3** + Ms_2O	**24** (31:4:65)[g]	50
22	**3** + Ts_2O	**18** (50:16:34)[j]	70
23	**8** + Ts_2O	**20**[k,l]	35[d]

[a] Anisole (**2**), toluene (**3**), metaxylene (**4**), paraxylene (**5**), benzene (**6**), fluorobenzene (**7**), chlorobenzene (**8**), bromobenzene (**9**); $ArH/RSO_2X = 2:1$ (mol); all reactions were carried out at 120 °C except for entry 11 (90 °C). [b] Catalyst: **1b**, 10 mol % (entries 5–7,10–13,19–23); 5 mol % (entries 1–4,8,14–18); 1 mol % (entry 9). [c] Reaction time: 1 h (entries 1,3,4); 1.5 h (entries 2,8,14,16–18); 3 h (entry 11); 4 h (entries 21,22); 5 h (entries 5–7,10,12,13, 19,23); 6 h (entry 15,20); 7 h (entry 9). [d] Determined by GC. [e] Nonoptimized yield for the isolated product except for entries 10,13,23. [f] These reactions have been carried out in an autoclave. [g–k] Various isomers: (2:3:4)[g], (2,4)[h], (2,5)[i], (2,4′:3,4′:4,4′)[j], (4:4′)[k]. [l] No other isomers could be detected.

case of the sulfonylation of toluene, **1b** remains efficient at 1 mol % (entry 9).

Finally, we have studied the action of various sulfonylating reagents on toluene. We chose sulfonyl chlorides (Table 2, entries 14,16–20) and sulfonic anhydrides (entries 21,22) for this study. Although the latter are known to be less reactive than the corresponding sulfonyl chlorides, convenient yields were obtained with Ms_2O or Ts_2O (entries 21,22) compared with MsCl and TsCl (entries 8,19). This difference was more strongly marked in the case of the sulfonylation of chlorobenzene with TsCl and Ts_2O (entries 12,23). Weaker yields were obtained with alkylsulfonyl chlorides MsCl and ^{n}BuSO$_2$Cl (entries 19,20) with respect to arylsulfonyl chlorides.

The reactions have been carried out using an excess of aromatic substrate with respect to the sulfonylation reagent (2:1 mol), without added solvent, in an open reactor heated by a thermostated oil bath at 120 °C, with the exception of the sulfonylation of the volatile fluorobenzene (90 °C) (Table 2, entry 11). From volatile and weakly reactive benzene, the reaction requires a temperature of 120 °C and, consequently, the use of an autoclave (Table 2, entries 5,10).

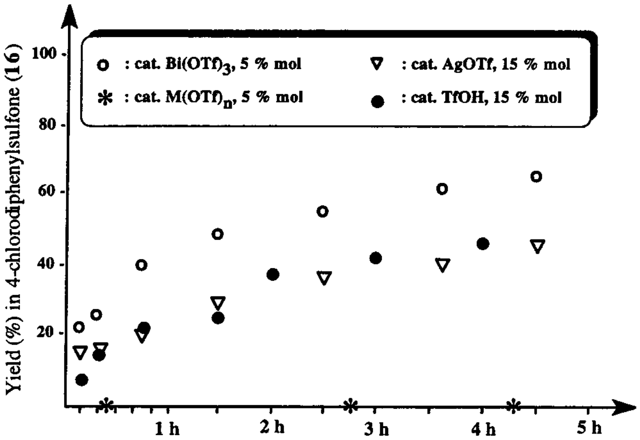
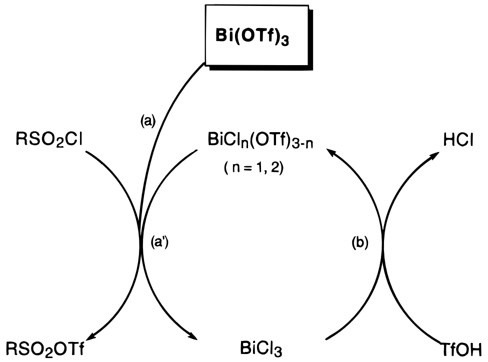


Figure 1. Catalysis of the benzenesulfonylation of **8**. Conditions: temp. 120 °C; benzenesulfonyl chloride (1 equiv), **8** (2 equiv), catalyst [M = Sc, Yb (n = 3); Ce, Hf (n = 4)]; yield based on $PhSO_2Cl$.

Scheme 1



From a mechanistic point of view, as we reported in a recent paper,[10e] **1b** was prone to give ligand exchange with acyl chlorides, leading to trifluoromethanesulfonic carboxylic anhydrides (RCOOTf), which are known to be strong acylating reagents.[12] Metal triflates that do not give this exchange reaction (Sc and other rare earth ones) are not efficient catalysts of the FC acylation of nonactivated aromatics by acyl chlorides.[10d,e] By analogy with this previous work, we compared the catalytic activity of some metallic triflates including **1b** for the sulfonylation of a deactivated substrate, chlorobenzene (**8**), by $PhSO_2Cl$. None of the metallic triflates tested (Sc, Ce, Yb, and Hf) proved to be efficient. Only AgOTf and **1b** exhibited catalytic activity, the latter being more effective (Figure 1). Effenberger and Hutchmacher have shown that, in the presence of an arylsulfonyl bromide, AgOTf gives a triflate/bromide exchange with formation of an unstable (but observable at low temperature) trifluoromethanesulfonic arenesulfonic anhydride ($ArSO_2OTf$), trapped by reaction with an arene.[11] A similar triflate/chloride exchange (eq 2, M = Ag) occurs at higher

$$M(OTf)_n + n\ RSO_2Cl \longrightarrow MCl_n + n\ RSO_2OTf \qquad (2)$$

$$M = Ag\ (n{=}1),\ Bi\ (n{=}3)$$

temperature (above 50 °C), and the trapping of $ArSO_2$-OTf has been reported by the same authors to be more difficult (20% from $PhSO_2Cl$ by reaction with acetonitrile).[5a,11] In the presence of a sulfonyl chloride, we have proved that **1b** also gives a triflate/chloride exchange (eq 2, M = Bi), contrary to Sc, Ce, Yb, or Hf triflates. Effectively, **1b** reacted with TsCl above 50 °C giving $BiCl_3$, *p*-toluenesulfonic, and triflic anhydrides.[13] These anhydrides correspond to the previously reported thermal disproportionation products of the mixed sulfonic anhydride RSO_2OTf (eq 3a, R = Ts).[5a,11] This TfO^-/Cl^-

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(12) Effenberger, F.; Epple, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 299.

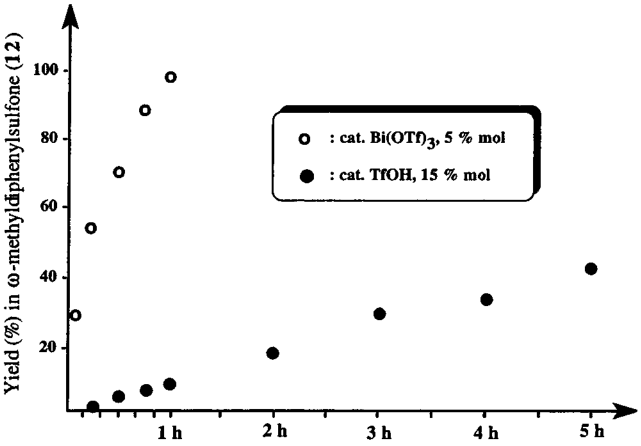
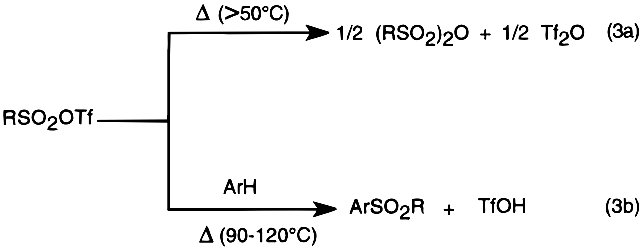


Figure 2. Catalysis of the benzenesulfonylation of **3**. Conditions: temp. 120 °C; benzenesulfonyl chloride (1 equiv), **3** (5 equiv), catalyst; yield based on $PhSO_2Cl$.

exchange is probably the first step of the reaction, which leads to the sulfonylating agent RSO_2OTf (Scheme 1, path a).



In a second step, RSO_2OTf might react with an arene before decomposition to produce the sulfone $ArSO_2R$ and triflic acid (eq 3b). Consequently, when the reaction is initiated by AgOTf, the catalysis could be attributed to TfOH,[5a] as this acid does not react with the AgCl produced to regenerate AgOTf. This hypothesis is supported by the result obtained when TfOH (15 mol %) is used to catalyze the same reaction (**8** + $PhSO_2Cl$), i.e., identical to that of AgOTf (15 mol %) (Figure 1).

Compared with our previous work on FC acylation,[10e] it is surprising that **1b** (5 mol %) exhibited a stronger activity than AgOTf (15 mol %) or TfOH (15 mol %) in the sulfonylation of chlorobenzene (**8**) by $PhSO_2Cl$ (Figure 1). Therefore, we have carried out sulfonylation of **8** by another reagent, 4-fluorobenzenesulfonyl chloride, using in one case 15 mol % of TfOH (120 °C, 6 h), and in the second case 5 mol % of **1b** (Table 2, entry 15). The yields in sulfone **22** were 25% with TfOH and 52% with **1b**. This difference of catalytic activity between **1b** and TfOH is still more clear in the case of the sulfonylation of toluene (Figure 2). To explain this difference we hypothesize that **1a** (as a result of eq 2) might be a cocatalyst. Because we have proved above that **1a** alone is not a catalyst of the reaction between **8** and $PhSO_2Cl$ (Table 1, entry 3), we have considered another possibility, the formation of RSO_2OTf by two consecutive reactions involving the bismuth atom: (i) a chloride/triflate exchange between **1a** and TfOH resulting in the formation of mixed compounds $BiCl_n(OTf)_{3-n}$, mainly $n = 1$[14] (third step) (Scheme 1, path b) and (ii) the latter leading to RSO_2OTf and **1a** by reaction with RSO_2Cl, as in eq 2 (Scheme 1, path a′).

If such a mechanism is correct, and if the first exchange reaction (path a) is fast, the reaction of an arene with $PhSO_2Cl$ carried out in the presence of **1a** (5 mol %) + TfOH (15 mol %) should not lead to the kinetic curve obtained with TfOH (15 mol %) but to the one observed when **1b** (5 mol %) was employed. Effectively, the catalytic system **1a** (5 mol %) + TfOH (15 mol %) used for the benzenesulfonylation of **3** and **8** led to the same kinetic curve as those obtained with **1b** (5 mol %) (Figures 1 and 2).

Because **1b** is able to generate in situ a strong sulfonylating reagent (RSO_2OTf), it is easy to explain the higher efficiency of **1b** toward **1a** in the FC sulfonylation reaction. We propose that bismuth(III) chloride (**1a**) activates the sulfonyl chlorides by coordination with the sulfoxide bond(s); a similar activation was proved in the case of acyl chlorides.[10b] In fact, the difference in efficiency of these two catalysts **1a** and **1b** in the FC acylation[10] and FC sulfonylation reactions is comparable.

The alkylated mixed anhydrides RSO_2OTf are less stable than the aromatic $ArSO_2OTf$ compounds.[5a] Compared to the reaction of **3** with arylsulfonyl chlorides (Table 2, entries 2,8,14,16−18), alkylsulfonyl chlorides gave weaker yields (Table 2, entries 19,20), which may be due to their known heterolytic dissociation[11] and subsequent formation of the inactive alkyl triflates.[15]

Concerning the sulfonic anhydrides Ms_2O and Ts_2O, their reactivity in the presence of **1b** is lower than that of the corresponding chlorides [Table 2, entries 8 (5 mol % of **1b**; 1.5 h; 80% yield) and 22 (10 mol % of **1b**; 4 h; 70% yield) and entries 12 (10 mol % of **1b**; 5 h; 73% yield) and 23 (10 mol % of **1b**; 5 h; 35% yield)]. This is indicative of a different catalytic mechanism for these two reagents, without formation of the same intermediate RSO_2OTf. Like carboxylic anhydrides,[10e] the electrophilic activity of sulfonic anhydrides is probably enhanced by complexation with the Lewis acid **1b**. An example of intramolecular coordination of a sulfonyl group with a bismuth atom has previously been described.[16] Silver triflate, which does not give any acylation reaction with carboxylic anhydrides,[10e] is totally inactive for the sulfonylation

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(13) From a sulfonyl chloride, the TfO^-/Cl^- exchange reaction with **1b**, as with AgOTf,[5a,11] takes place above the decomposition temperature of the mixed sulfonic anhydride RSO_2OTf (eq 3a). Consequently, proof of this reaction is limited to the identification of symmetrical anhydrides $(RSO_2)_2O$ and Tf_2O. This identification has been carried out from mixtures, AgOTf + TsCl on one hand and **1b** + 3 TsCl on the other hand, from room temperature to 80 °C, using nitromethane as solvent. The substitution of TsCl by Ts_2O has been characterized by ^1H NMR (300 MHz, solvent $MeNO_2$, internal reference CD_3NO_2) aromatic protons (divided doublets, $^3J = 7.5-8.2$ Hz): TsCl, δ 7.49 and 7.90; Ts_2O, δ 7.36 and 7.66; Me (s) TsCl, δ 2.45; Ts_2O, δ 2.42 ppm. For AgOTf and **1b**, the exchange reaction begins between room temperature and 40 °C and is nearly quantitative at 80 °C.

(14) Compound **1a** reacts with fluorosulfonic acid; however, an excess of this acid is needed to obtain $Bi(SO_3F)_3$ as the mixed product $Bi(SO_3F)_2Cl$ is more easily formed: Paul, R. C.; Singh, S.; Kumar, R. C.; Sharma, R. D.; Verma, R. D. *Ind. J. Chem.* **1979**, 273. The same reaction between **1a** and TfOH (1:2 molar ratio, solvent toluene, 60 °C, 10 min) gave a new bismuth complex. Immediatly after reaction, the solvent was removed under vacuum. Analysis of the product showed that 70% of the triflate introduced was bonded to the bismuth atoms. In a second experiment conducted with a 1:3 molar ratio of **1a** and TfOH (the molar ratio of the sulfonylation reaction) (100 °C, 1 h), the analysis of the bismuth complex (by gravimetry for Cl^- and ^{19}F NMR for TfO^-) showed a Cl^-/TfO^- ratio equal to 1:2. We assigned the formula $BiCl(OTf)_2$ to the product by analogy with the reaction of fluorosulfonic acid and **1a**. However, during further analyses (IR, XRD), this mixed compound disproportionated into symmetrical derivatives **1a** and **1b**.

(15) Booth, B. L.; Haszeldine, R. N.; Khosrow, L. *J. Chem. Soc., Perkin Trans 1* **1980**, 2887.

(16) Suzuki, H.; Murafugi, T.; Azuma, N. *J. Chem. Soc., Perkin Trans 1* **1993**, 1169.

reactions between **3** or **8** with Ms_2O or Ts_2O. This is explained by the inhability of AgOTf to undergo exchange reactions or participate in coordination with the sulfonic anhydrides.

Conclusion

The use of bismuth(III) chloride (**1a**) and triflate (**1b**) in the field of FC reactions has been extended to the sulfonylation of arenes. Compound **1b** appears to be efficient for the preparation of aromatic sulfones $ArSO_2$-Ar′ and $ArSO_2R$. As observed during the catalytic FC acylation reaction, **1b** has two behavior patterns ("chameleon" catalyst)[10e] depending upon the sulfonylation reagent employed, sulfonyl chloride or sulfonic anhydride. The proposed mechanism with sulfonyl chlorides ($Ar'SO_2$-Cl or RSO_2Cl) involves a ligand exchange (TfO^-/Cl^-) at the bismuth atom, leading to **1a** and a mixed sulfonic anhydride ($Ar'SO_2OTf$ or RSO_2OTf) (first step), which is responsible for the sulfonylation of the aromatic substrate with formation of TfOH (second step). This latter, poor activator of sulfonyl chlorides reacts preferentially with **1a**, taking back the triflate groups on the bismuth atom (third step). Though this reaction is partial, it explains the better catalytic activity of **1b** toward AgOTf and TfOH. Other metallic triflates tested (Sc, Ce, Yb, and Hf), which do not give the TfO^-/Cl^- exchange, proved to be inactive catalysts.

From sulfonic anhydrides, their activation would involve a coordination complex with **1a** or **1b**. No catalytic power has been observed for the other metallic triflates (Ag, Sc, etc.) used with these electrophiles.

In conclusion, because bismuth is the least toxic of the heavy elements,[17] **1b** is a safe alternative to the use of the very hygroscopic and corrosive triflic acid in FC reactions such as the acylation or sulfonylation of arenes.

Experimental Section

General. All starting materials, including metallic triflates, with the exception of bismuth(III) trifluoromethanesulfonate (**1b**), were commercially available (from Aldrich). All products of sulfonylation reactions were identified and their isomeric compositions were determined by a comparison of their spectral data (NMR, GC−MS) with those of authentic samples. GC experiments were carried out on a Hewlett-Packard 6890 chromatograph equipped with a 30 m × 0.32 mm column (methyl silicone doped with 5% phenyl silicone, 0.25 μm). GC−MS experiments were performed on a Hewlett-Packard MS 5989 apparatus (EI 70 eV) equipped with a GC 5890 chromatograph.

Bismuth(III) Trifluoromethanesulfonate (1b). This compound was prepared as previously described from triphenylbismuth and triflic acid and characterized by its NMR and IR data.[10c,18] The catalyst used for the reactions described here was a mixture containing mainly anhydrous **1b** with weakly hydrated forms,[19,20] i.e., a mixture containing about 5% by weight of water (by TGA).[20] An amount of water higher than 10% by weight caused a significant fall in the reaction yield.

Typical Procedure for the Synthesis of a Sulfone, Phenyl Tolyl Sulfone (12). From Toluene (3) and Benzenesulfonyl Chloride. In a 100 mL flask were introduced **1b** (1.32 g, 2 mmol), toluene (7.38 g, 80 mmol), and benzenesulfonyl chloride (7.06 g, 40 mmol). The flask was equipped with a condenser, immersed in an oil bath, and heated for 1.5 h at 120 °C. After the mixture cooled, 20 mL of dichloromethane and 20 mL of 6% aqueous HCl were added. The products were extracted with dichloromethane (2 × 20 mL). The combined organic phases were dried over magnesium sulfate and concentrated. The crude mixture was recrystallized from dichloromethane/pentane to give 7.79 g of sulfone **12** (84% yield) as a white solid, which identified with a pure sample.[21] ^1H NMR ($CDCl_3$): δ 2.36 and 2.42 (2s, *p*-**12** and *o*-**12**), 7.1−8.3 (m, ar. protons). GC (temperature conditions 160 to 300 °C, 20 °C/min): 3 peaks at 5.86, 5.92, and 6.14 min (*o*-**12**/*m*-**12**/*p*-**12** = 37/6/57). GC−MS *m/z*: phenyl-*o*-tolyl sulfone [*7018-84-0*]: 232 (M^+, 31), 214 (53), 167 (44), 166 (94), 165 (36), 137 (43), 91 (48), 90 (30), 89 (42), 78 (26), 77(*100*), 65 (89), 63 (25), 51 (78), 50 (23); phenyl-*p*-tolyl sulfone [*640-57-3*]: 232 (M^+, 68), 139 (96), 125 (71), 107(*100*), 91 (56), 79 (26), 77 (84), 65 (60), 51 (61).

From Benzene (6) and Tosyl Chloride. To a 200 mL stainless steel autoclave were introduced **1b** (2.63 g, 4 mmol), benzene (7.36 g, 80 mmol), and tosyl chloride (7.62 g, 40 mmol). The mixture was heated for 5 h at 120 °C. After a similar workup, 5.84 g (63% yield) of phenyl-*p*-tolyl sulfone **12** was isolated. Mp: 125 °C. [lit.[21] 125 °C].

Typical Procedure for Kinetic Experiments (Figures 1 and 2). Compound **1b** (656 mg, 1 mmol), benzenesulfonyl chloride (3.53 g, 20 mmol), hexadecane (1.81 g, 8 mmol), and **8** (4.5 g, 40 mmol) were placed in a 50 mL round-bottomed flask equipped with a condenser and heated in an oil bath (120 °C). The evolution of the reaction was monitored by analyzing aliquots (quenched with triethylamine) by GC. The yield of (chlorophenyl)phenyl sulfone (**16**) was determined using hexadecane as an internal standard.

For the catalysis of the benzenesulfonylation of **3** (Figure 2) the procedure was the same with the exception of a different ratio of reagents (**3**:$PhSO_2Cl$ = 5:1) being employed.

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Supporting Information Available: Gas chromatographic, GC−MS, and ^1H NMR analyses of sulfones **10**−**25**. This material is available free of charge via the Internat at http://pubs.acs.org.

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