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

Sigrid Répichet, Christophe Le Roux,
Pierre Hernandez, and Jacques Dubac*

*Hétérochimie Fondamentale et Appliquée (UPRES(A) 5069
CNRS), Université Paul-Sabatier, 118 route de Narbonne,
31062 Toulouse Cedex, France*

Jean-Roger Desmurs

*Rhodia Organique Fine, Centre de Recherche de Lyon,
85 Avenue des Frères-Perret,
69192 Saint-Fons Cedex, France*

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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 Brønsted acids, for example polyphosphoric acid⁴ 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 acylation⁸ 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

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

entry	reaction ^{a,b}	product and isomers ^c	yield (%) ^c
1	2 + PhSO ₂ Cl	10 (43:7:50) ^d	22
2	3 + PhSO ₂ Cl	12 (32:6:62) ^d	8
3	8 + PhSO ₂ Cl	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 ₂ O	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.

acylation.¹⁰ In a *stoichiometric process* from arylsulfonyl bromides, silver triflate gives trifluoromethanesulfonic arenesulfonic anhydrides (ArSO₂OTf), 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*.



Catalyst: **1a** or **1b** (1–10% mol)

X = Cl or OSO₂R ; 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 PhSO₂Cl, 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 Ts₂O (entries 5,7). For the same reactions, the catalytic activity of **1b** was much higher, in particular for the reactions involving PhSO₂Cl 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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Table 2. Sulfonylation Reactions Catalyzed by Bismuth(III) Triflate (**1b**)

entry	reaction ^{a-c}	product and isomers ^d	yield (%) ^e
1	2 + PhSO ₂ Cl	10 (48:0:52) ^g	80
2	3 + PhSO ₂ Cl	12 (37:6:57) ^g	84
3	4 + PhSO ₂ Cl	13 ^{h,i}	90
4	5 + PhSO ₂ Cl	14 ^{i,l}	90
5	6 + PhSO ₂ Cl ^f	15	63
6	8 + PhSO ₂ Cl	16 (3:0:97) ^g	70
7	9 + PhSO ₂ Cl	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 ₆ H ₄ SO ₂ Cl	19 (41:7:52) ^j	80
15	8 + 4-F-C ₆ H ₄ SO ₂ Cl	22 ^{k,l}	52
16	3 + 4-Cl-C ₆ H ₄ SO ₂ Cl	20 (40:6:54) ^j	84
17	3 + 4-Bu-C ₆ H ₄ SO ₂ Cl	23 (28:4:68) ^j	90
18	3 + 4-MeO-C ₆ H ₄ SO ₂ Cl	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 ₂ O	24 (31:4:65) ^g	50
22	3 + Ts ₂ O	18 (50:16:34) ^j	70
23	8 + Ts ₂ O	20 ^{k,l}	35 ^d

^a Anisole (**2**), toluene (**3**), metaxylene (**4**), paraxylene (**5**), benzene (**6**), fluorobenzene (**7**), chlorobenzene (**8**), bromobenzene (**9**); ArH/RSO₂X = 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 Ms₂O or Ts₂O (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 Ts₂O (entries 12, 23). Weaker yields were obtained with alkylsulfonyl chlorides MsCl and ⁿBuSO₂Cl (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).

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)

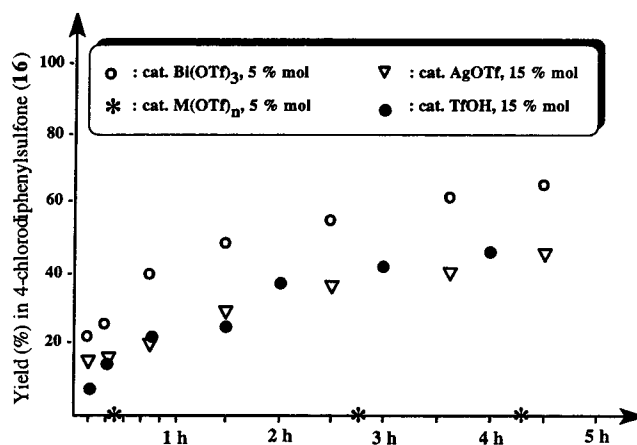
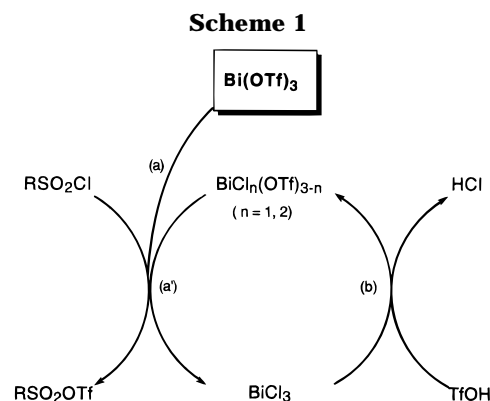
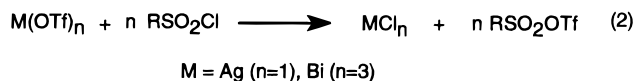


Figure 1. Catalysis of the benzenesulfonylation of **8**. Conditions: temp. 120 °C; benzenesulfonyl chloride (1 equiv), **8** (2 equiv), catalyst [M = Sc, Yb (*n* = 3); Ce, Hf (*n* = 4)]; yield based on PhSO₂Cl.



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 PhSO₂Cl. 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 (ArSO₂OTf), trapped by reaction with an arene.¹¹ A similar triflate/chloride exchange (eq 2, M = Ag) occurs at higher



temperature (above 50 °C), and the trapping of ArSO₂OTf has been reported by the same authors to be more difficult (20% from PhSO₂Cl 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 BiCl₃, *p*-toluenesulfonic, and triflic anhydrides.¹³ These anhydrides correspond to the previously reported thermal disproportionation products of the mixed sulfonic anhydride RSO₂OTf (eq 3a, R = Ts).^{5a,11} This TfO[−]/Cl[−]

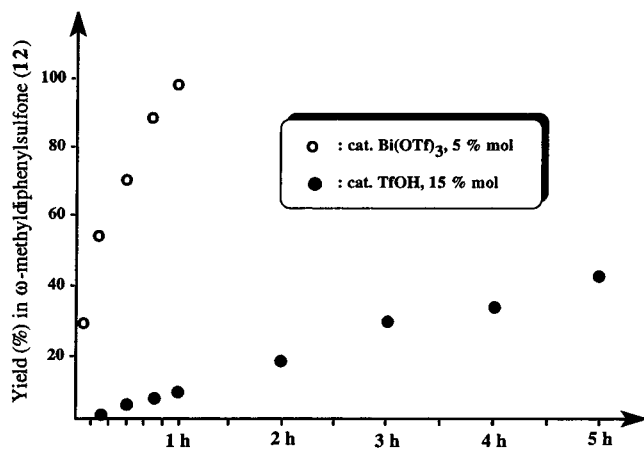
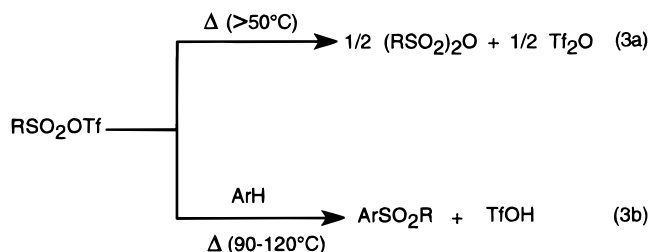


Figure 2. Catalysis of the benzenesulfonylation of **3**. Conditions: temp. 120 °C; benzenesulfonyl chloride (1 equiv), **3** (5 equiv), catalyst; yield based on PhSO₂Cl.

exchange is probably the first step of the reaction, which leads to the sulfonylating agent RSO₂OTf (Scheme 1, path a).



In a second step, RSO₂OTf might react with an arene before decomposition to produce the sulfone ArSO₂R 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** + PhSO₂Cl), 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 PhSO₂Cl (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

(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 RSO₂OTf (eq 3a). Consequently, proof of this reaction is limited to the identification of symmetrical anhydrides (RSO₂)₂O and Tf₂O. 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 Ts₂O has been characterized by ¹H NMR (300 MHz, solvent MeNO₂, internal reference CD₃NO₂) aromatic protons (divided doublets, ³J = 7.5–8.2 Hz): TsCl, δ 7.49 and 7.90; Ts₂O, δ 7.36 and 7.66; Me (s) TsCl, δ 2.45; Ts₂O, 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.

we have proved above that **1a** alone is not a catalyst of the reaction between **8** and PhSO₂Cl (Table 1, entry 3), we have considered another possibility, the formation of RSO₂OTf 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 = 1¹⁴ (third step) (Scheme 1, path b) and (ii) the latter leading to RSO₂OTf and **1a** by reaction with RSO₂Cl, 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 PhSO₂Cl 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 (RSO₂OTf), 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 acylation¹⁰ and FC sulfonylation reactions is comparable.

The alkylated mixed anhydrides RSO₂OTf are less stable than the aromatic ArSO₂OTf 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 dissociation¹¹ and subsequent formation of the inactive alkyl triflates.¹⁵

Concerning the sulfonic anhydrides Ms₂O and Ts₂O, 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 RSO₂OTf. 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

(14) Compound **1a** reacts with fluorosulfonic acid; however, an excess of this acid is needed to obtain Bi(SO₃F)₃ as the mixed product Bi(SO₃F)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. Immediately 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 ¹⁹F 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**.

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reactions between **3** or **8** with Ms_2O or Ts_2O . This is explained by the inability 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 $\text{ArSO}_2\text{-Ar'}$ 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 ($\text{Ar'SO}_2\text{-Cl}$ or RSO_2Cl) involves a ligand exchange (TfO^-/Cl^-) at the bismuth atom, leading to **1a** and a mixed sulfonic anhydride ($\text{Ar'SO}_2\text{OTf}$ 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 \times 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 triphenylbis-

moth 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 \times 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 Internet at <http://pubs.acs.org>.

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