Total Synergistic Effect between Triflic Acid and Bismuth(III) or Antimony(III) Chlorides in Catalysis of the Methanesulfonylation of Arenes

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Keywords: Alkylsulfonylation / Catalysis / Friedel–Crafts reaction / Triflic acid

A total synergistic effect between bismuth(III) or antimony(III) chlorides and triflic acid has been observed in the Friedel–Crafts methanesulfonylation of arenes and has resulted in the development of the first efficient catalytic systems usable for the methanesulfonylation of both activated and deactivated arenes. A proposed mechanism to explain the observed effects is also discussed.

Introduction

Trifluoromethanesulfonic acid (**1**) is a well known and efficient superacid catalyst for Friedel–Crafts reactions of arenes.[1] Its catalytic activity can be enhanced by complexation with metallic halides[1] or triflates.[2] In addition, we recently reported that the catalytic activity of **1**, which is a poor catalyst for Friedel–Crafts arylsulfonylation,[3] could be improved by doping with $BiCl_3$ (**2**).[4] Although numerous catalysts for Friedel–Crafts arylsulfonylation of arenes have been reported,[5] few catalytic methods for the preparation of alkyl sulfones are available.[5f,5h,6] Here we report that extreme synergy between **1** and **2** (system **A**) or between **1** and $SbCl_3$ (**3**) (system **B**) has resulted in the first efficient catalytic system for the methanesulfonylation of arenes with the commercially available methanesulfonyl chloride.

Results and Discussion

Bismuth(III) chloride (**2**)[5f] is not an efficient catalyst for the arylsulfonylation of arenes and, just as **1**[3] and **3**, proved to be inactive for the methanesulfonylation of toluene (**4**) (Table 1, Entry 1) and a variety of other arenes such as mesitylene (**5**), *o*-xylene (**6**), *m*-xylene (**7**), *p*-xylene (**8**), fluorobenzene (**9**), benzene (**10**), chlorobenzene (**11**), *o*-dichlorobenzene (**12**), 1,3-difluorobenzene (**13**), *o*-fluorotoluene (**14**), *m*-fluorotoluene (**15**) and *p*-fluorotoluene (**16**) (for purposes of clarity these results are not shown in the table). When system **A** or system **B** was used, however, an exothermic reaction occurred and a mixture of methyltolylsulfones (**17**) was obtained in almost quantitative yields, accompanied by the release of hydrogen chloride (Table 1, Entries 2, 3). From testing of different ratios of **1**, **2** and **3** in the two systems it appeared that 10% mol is an optimum amount for each component of these systems. The yields of the sulfones (**17**–**29**) obtained from various arenes (**4**–**16**) and methanesulfonyl chloride[7] are summarized in Table 1.

From these results one can conclude that system **A** is able to catalyse the methanesulfonylation of various arenes efficiently. In the case of *m*-xylene (**7**), the yield of the sulfone is lowered by the formation of tarry products, as previously reported.[9] Moreover, our results obtained for the methanesulfonylation of *p*-xylene (**8**) with system **A** (Table 1, Entry 10) are similar to those recently reported by Olah et al. with MsOH and Nafion-H, while system **B** proved to be less efficient (Table 1, Entry 11).[10] In analogy with our previous work, we propose the mechanism shown in Scheme 1, which is supported by the following observations: Step (a) concerns the reaction between **1** and **2** (system **A**), which gives rise to the mixed bismuth chlorotriflates $BiCl_n(OTf)_{3-n}$.[5f,11] Step (b) involves the ligand exchange between the mixed bismuth(III) chlorotriflate[13] and methanesulfonyl chloride, resulting in the regeneration of **2** and production of the mixed trifluoromethanesulfonic methanesulfonic anhydride ($MeSO_2OTf$) (**30**).[14] In step (c), **30** reacts with the arene to generate **1** and the methylsulfone. A similar mechanism is involved in the case of system

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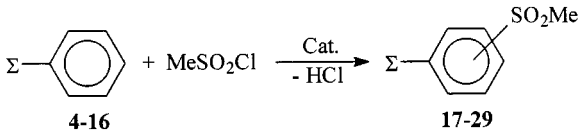
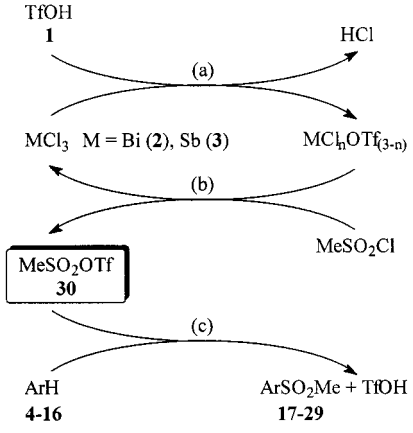
Table 1. Catalytic methanesulfonylation of arenes



4-16 **17-29**

Entry	ArH[a]	Cat.	Temp. °C,[b] (time, days)	Product[c] (yield, %)[d]
1	**4**	**1** or **2** or **3**	120 (1.5)	**17** (0)
2	**4**	**A**[e]	120 (1.5)	**17** (92)
3	**4**	**B**[f]	120 (1.5)	**17** (92)
4	**5**	**A**	120 (0.7)	**18** (80)
5	**5**	**B**	120 (0.7)	**18** (8)
6	**6**	**A**	120 (3)	**19** (87)
7	**6**	**B**	120 (3)	**19** (18)
8	**7**	**A**	120 (1)	**20** (31)
9	**7**	**B**	120 (1)	**20** (12)
10	**8**	**A**	120 (3)	**21** (91)
11	**8**	**B**	120 (3)	**21** (45)
12	**9**	**A**	105 (3)	**22** (0)
13	**9**	**B**	105 (3)	**22** (97)
14	**10**	**A**	105 (6)	**23** (94)
15	**10**	**B**	105 (6)	**23** (91)
16	**11**	**A**	125 (7)	**24** (78)
17	**11**	**B**	105 (7)	**24** (73)
18	**12**	**A**	130 (7)	**25** (19)
19	**12**	**B**	130 (7)	**25** (13)
20	**13**	**B**	110 (7)	**26** (93)
21	**14**	**B**	120 (4)	**27** (87)
22	**15**	**B**	120 (7)	**28** (71)
23	**16**	**B**	120 (7)	**29** (89)

[a] ArH/$MeSO_2Cl$/cat. = 3:1/0.1 mol %, arenes are: toluene (**4**), mesitylene (**5**), *o*-xylene (**6**), *m*-xylene (**7**), *p*-xylene (**8**), fluorobenzene (**9**), benzene (**10**), chlorobenzene (**11**), *o*-dichlorobenzene (**12**), *m*-difluorobenzene (**13**), *o*-fluorotoluene (**14**), *m*-fluorotoluene (**15**), and *p*-fluorotoluene (**16**). [b] Temperature of the oil bath. [c] Products are: mixture of methyl methylphenyl sulfones **17**, methyl 2,4,6-trimethylphenyl sulfone (**18**), mixture of dimethylphenyl methyl sulfones **19**−**21**, mixture of fluorophenyl methyl sulfones **22**, methyl phenyl sulfone (**23**), mixture of chlorophenyl methyl sulfones **24**, mixture of dichlorophenyl methyl sulfones **25**, mixture of difluorophenyl methyl sulfones **26**, mixture of fluoromethylphenyl methyl sulfones **27**−**29**. [d] Isolated yield in $ArSO_2Me$; for the determination of isomer ratios see Exp. Sect. [e] Cat. **A** = $BiCl_3$/TfOH. [f] Cat. **B** = $SbCl_3$/TfOH.



Scheme 1

B, the mixed antimony chlorotriflate compound being $SbCl_2OTf$.[12] Interestingly, with system **B** almost no reaction takes place in the case of **5** (Entry 5), while this system proved to be efficient with fluorobenzene (**9**) (Entry 13). Mesitylene (**5**) is a strong π donor arene capable of generating Menschutkin complexes, which are most probably involved in deactivation of the catalyst.[15] When 10% mol of pure $SbCl_2OTf$[12] was used in the methanesulfonylation of **5**, a 9% yield of methyl 2′,4′,6′-trimethylphenyl sulfone (**18**) was isolated (same conditions than for Entry 5), indicating that the deactivation of the system **B** arises from the inhibition of the reaction between **1** and **3** through its complexation with **5** (step a). In the case of **9**, the difference between the two systems stems from the solubility of **3** in aromatics (a consequence of the respective ionic and covalent natures of **2** and **3**).[16] System **B** was therefore used for the methanesulfonylation of various fluoroarenes (Table 1, Entries 21−23).

It may be noted that the reaction times for both systems are quite long, and since the amount of the alkyl sulfone increases during the course of the reaction, one might hypothesize that this compound could interact strongly with **2** or **3** or the mixed chlorotriflate intermediate species, resulting in a progressive deactivation of the catalytic system. Indeed, when the methanesulfonylation of **4** (same conditions as for Entries 2 and 3) was conducted in the presence of 0.6 equivalent of the sulfone **18**, the yield of **17** dropped to 15% in both cases. An infrared study conducted in toluene ([*c*]= 86 mM) revealed that **18** ($\nu SO_2^{asym.}$ = 1318 cm^{-1}, $\nu SO_2^{sym.}$ = 1151 cm^{-1}) is strongly complexed by **2** and **3**, resulting in a shift of both symmetrical and unsymmetrical absorption bands of SO_2 to lower frequencies (for the mixture **18**+**2**: $\nu SO_2^{asym.}$= 1295 cm^{-1}, $\nu SO_2^{sym.}$= 1132 cm^{-1}; for the mixture **18**+**3**: $\nu SO_2^{asym.}$ = 1301 cm^{-1}, $\nu SO_2^{sym.}$ = 1142 cm^{-1}). In addition, the respective amounts of free and complexed sulfone were estimated by deconvolution calculations.[17]

Conclusion

In conclusion, total synergistic effects between triflic acid and bismuth(III) chloride or antimony(III) chloride in the catalytic Friedel−Crafts methanesulfonylation of arenes have been observed, these metal chlorides acting as shuttles for triflate ligands. The screening of other catalytic systems is currently underway.

Experimental Section

General Remarks: All experiments were carried out under argon by use of standard Schlenk techniques. Arenes were purified by conventional methods, and methanesulfonyl chloride was used as received. Triflic acid was distilled twice over pure sulfuric acid, stored under argon and added to the reaction mixture by syringe. Commercially available bismuth(III) and antimony(III) chlorides were dried by the following procedure: i) heating at reflux over thionyl chloride for 1 h, ii) evaporation of thionyl chloride under

reduced pressure (0.05 mm of Hg) at room temp., and iii) removal of the traces of thionyl chloride under reduced pressure (0.05 mm of Hg) at 80 °C [for bismuth(III) chloride] or 50 °C [for antimony(III) chloride]. GC experiments were carried out with a Hewlett−Packard 6890 chromatograph fitted with a 30 × 0.32 × 0.25 column (methyl silicone doped with 5% phenyl silicone). GC-MS experiments were performed with a Hewlett−Packard MS 5989 apparatus (EI 70 eV) fitted with a Hewlett−Packard 6890 chromatograph. ^{1}H NMR spectra were recorded with a Bruker AM 400 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ = 7.26 ppm). ^{13}C NMR spectra were recorded with a Bruker AM 400 spectrometer with complete proton decoupling. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform: δ = 77.0 ppm). ^{19}F NMR spectra were recorded on Bruker AC 200 or ARX 400 spectrometers. Chemical shifts are reported in ppm with trifluoroacetic acid as the internal standard. Resonances were assigned by standard 2D NMR correlation experiments (COSY, HMBC, HMQC). All known compounds (**18**, **23**) had characteristics identical to those previously reported.[6c,18,19]

Methyl 2-Methylphenyl Sulfone (17a), Methyl 3-Methylphenyl Sulfone (17b) and Methyl 4-Methylphenyl Sulfone (17c):[6c,18] GC: 3 peaks, t_R = 4.55, 4.63 and 4.75 min (**17a/17b/17c** = 50:16:34). MS (EI): *m/z* (%) of **17a** = 170 (50) [M$^{+\cdot}$], 155 (15), 107 (36), 91 (100), 65 (52), 39 (34). MS (EI): *m/z* (%) of **17b** = 170 (43) [M$^{+\cdot}$], 155 (18), 107 (33), 91 (100), 65 (66), 39 (51). MS (EI): *m/z* (%) of **17c** = 170 (32) [M$^{+\cdot}$], 155 (31), 107 (33), 91 (100), 65 (57), 39 (45). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.40 (s, ArMe, **17c**), 2.41 (s, ArMe, **17b**), 2.65 (s, ArMe, **17a**), 3.18 (s, SO_2Me, **17c**), 3.20 (s, SO_2Me, **17b**), 3.21 (s, SO_2Me, **17a**), 7.28−7.36 (m, 4 H, H^{1,5}, **17a** and H^{3,5}, **17c**), 7.40−7.42 (m, 2 H, H^{4,5}, **17b**), 7.47 (td, *J* = 1.4, 7.5 Hz, 1 H, H^3, **17a**), 7.67−7.71 (m, 2 H, H^{2,6}, **17b**), 7.75−7.80 (m, 2 H, H^{2,6}, **17c**), 7.97−8.00 (dd, *J* = 1.4, 7.9 Hz, 1 H, H^6, **17a**) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.2 (C^2−*Me*,**17a**), 21.3 (C^3−*Me*, **17b**), 21.6 (C^4−*Me*, **17c**), 43.7 (C−SO_2*Me*, **17a**), 44.5 (C−SO_2*Me*, **17b**), 44.6 (C−SO_2*Me*, **17c**), 124.4 (C^{2}H, **17b**), 126.7 (C^{5}H, **17a**), 127.3 (C^{2,6}H, **17c**), 127.6 (C^{6}H, **17b**), 129.1 (C^{6}H, **17a**), 129.3 (C$^{4or\ 5}$H, **17b**), 130.0 (C^{3,5}H, **17c**), 132.8 (C^{3}H, **17a**), 133.8 (C^{4}H, **17a**), 134.5 (C$^{4\ or\ 5}$H, **17b**), 137.5 and 137.7 (C^2 of **17a** and C^3 of **17b**), 138.7 (C^1, **17c**), 139.7 (C^1, **17a**), 140.4 (C^1, **17b**), 144.7 (C^4, **17c**) ppm.

3,4-Dimethylphenyl Methyl Sulfone (19a) and 2,3-Dimethylphenyl Methyl Sulfone (19b): GC: 2 peaks, t_R = 5.33, 5.45 min (ratio 51:49); For the peak at 5.33 min. MS (EI): *m/z* (%) = 184 (81) [M$^{+\cdot}$], 169 (17), 121 (54), 105 (100), 104 (24), 103 (40), 91 (22), 79 (47), 78 (46), 77 (64), 65 (14), 51 (19), 39 (19); For the peak at 5.45 min. MS (EI): *m/z* (%) = 184 (59) [M$^{+\cdot}$], 169 (43), 121 (41), 105 (100), 103 (25), 91 (15), 79 (49), 78 (18), 77 (53), 65 (11), 63 (21), 51 (20), 39 (21). ^{1}H NMR of the mixture of **19a** and **19b** (400 MHz, $CDCl_3$): δ = 2.27 and 2.28 (2s, C^{3,4}−*Me*, of **19a** and C^3−*Me*, of **19b**), 2.55 (s, C^4−*Me*, **19b**), 2.95 and 3.02 (2s, SO_2Me of **19a** and **19b**), 7.19 (m, C^{5}H, **19b**), 7.22 (d, *J* = 7.7 Hz, C^{5}H, **19a**), 7.35 (dd, *J* = 0.4, 7.5 Hz, C^{4}H, **19b**), 7.57 (dd, *J* = 1.8, 8.0 Hz, C^{6}H, **19a**), 7.61 (m, C^{2}H, **19a**), 7.84 (m, C^{6}H, **19b**) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.3, 19.9, 20.2, 20.6 (C−*Me* of **19a** and **19b**), 44.1, 44.8 (C−SO_2*Me* of **19a** and **19b**), 124.9, 126.2, 127.1, 128.2, 130.6, 135.4 (*C*H phenyl of **19a** and **19b**), 136.0, 138.0, 138.3, 139.2, 139.8, 143.5 (*C*−Me and *C*−SO_2Me of **19a** and **19b**) ppm.

2,4-Dimethylphenyl Methyl Sulfone (20a), 2,6-Dimethylphenyl Methyl Sulfone (20b) and 3,5-Dimethylphenyl Methyl Sulfone (20c): GC: 2 peaks, t_R = 4.94 (**20b**), 5.16 (**20a**) min (ratio **1**:**2** = 81:19). MS (EI): *m/z* (%) of **20a** = 184 (72) [M$^{+\cdot}$], 169 (35), 121 (45), 105 (100), 104 (11), 103 (31), 91 (24), 79 (42), 78 (29), 77 (59), 65 (15), 63 (18), 51 (21), 39 (23). MS (EI): *m/z* (%) of **20b**: 184 (100) [M$^{+\cdot}$], 169 (13), 121 (73), 105 (87), 104 (34), 103 (54), 91 (29), 79 (44), 78 (66), 77 (71), 65 (23), 63 (23), 51 (29), 39 (32). ^{1}H NMR of the mixture of **20a**, **20b** and **20c** (400 MHz, $CDCl_3$): δ = 2.35 (s, C2−*Me*, **20a**), 2.36 (s, C^{3,5}−*Me*, **20c**), 2.63 (s, C^4−Me, **20a**), 2.67 (s, C^{2,6}−*Me*, **20b**), 2.99 (s, SO_2Me, **20c**), 3.01 (s, SO_2Me, **20a**), 3.03 (s, SO_2Me, **20b**), 6.95−7.15 (m, C^{3,5}H, **20a** and C^{3,5}H, **20b**), 7.21 (m, C^{4}H, **20c**), 7.29 (t, *J* = 7.7 Hz, C^{4}H, **20b**), 7.50 (s, C^{2,6}H, **20c**), 7.86 (d, *J* = 7.9 Hz, C^{6}H, **20a**); ratio **20a/20b/20c** estimated by ^{1}H NMR = 75:21:4. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3 (C^2*Me*, **20a**), 21.4 (C^{3,5}*Me*, **20c**), 21.5 (C^{4}Me, **20a**), 23.1 (C^{2,6}*Me*, **20b**), 44.0 (C−SO_2*Me*, **20a**), 44.4 (C−SO_2*Me*, **20b**), 44.6 (C−SO_2*Me*, **20c**), 125.0 (C^{2,6}H, **20c**), 127.5 (C^{5}H, **20a**), 129.5 (C^{6}H, **20a**), 131.7 (C^{3,5}H, **20b**), 132.9 (C^{4}H, **20b**), 133.6 (C^{3}H, **20a**), 135.5 (C^{4}H, **20c**), 136.0 (*C*−SO_2Me, **20a**), 137.5 (*C*^{2}Me of **20a** and *C*−SO_2Me of **20b**), 139.7 (*C*^{2,6}Me, **20b**), 144.7 (*C*^{4}Me, **20a**).

2,5-Dimethylphenyl Methyl Sulfone (21): GC: t_R = 5.04 min. MS (EI): *m/z* (%) = 184 (94) [M$^{+\cdot}$], 135 (61), 169 (23), 121 (61), 105 (100), 104 (42), 103 (43), 79 (49), 78 (44), 77 (62), 51 (22), 39 (20). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, C^5*Me*), 2.62 (s, 3 H, C^2*Me*), 3.02 (s, 3 H, SO_2Me), 7.18 (d, *J* = 7.7 Hz, 1 H, C^{3}H), 7.28 (dd, *J* = 7.7, 1.5 Hz, 1 H, C^{4}H), 7.80 (m, 1 H, C^{6}H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (C^2−*Me*), 21.0 (C^5−*Me*), 43.8 (C−SO_2*Me*), 129.7 (C^{6}H), 132.8 (C^{3}H), 134.4 (*C*^{2}Me), 134.5 (C^{4}H), 136.9 (*C*^{5}Me), 138.4 (*C*−SO_2Me) ppm.

4-Fluorophenyl Methyl Sulfone (22a) and 2-Fluorophenyl Methyl Sulfone (22b): GC: 2 peaks, t_R = 3.75 (**22a**) and 3.92 (**2**) min (ratio **22a/b** = 76:24). MS (EI): *m/z* (%) of **22a**: 174 (24) [M$^{+\cdot}$], 159 (32), 112 (21), 111 (25), 95 (100), 83 (23), 75 (64), 50 (20), 39 (28). MS (EI): *m/z* (%) of **22b**: 174 (38) [M$^{+\cdot}$], 159 (35), 112 (57), 111 (25), 95 (100), 83 (27), 75 (72), 74 (19), 69 (21), 63 (20), 50 (23). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.05 (s, SO_2Me, **22a**), 3.21 (s, SO_2Me, **22b**), 7.17−7.40 (m, C^{3,5}H of **22a** and C^{3,4,5}H of **22b**), 7.65 (m, C^{6}H, **22b**), 7.95 (m, C^{2,6}H, **22a**) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 44.4 (d, *J* = 2.8 Hz, C−SO_2*Me*, **22b**), 45.1 (s, C−SO_2*Me*, **22a**), 117.2 (d, *J* = 22.9 Hz, C^{3,5}, **22a**), 117.8 (d, *J* = 21.3 Hz, C^3, **22b**), 125.5 (d, *J* = 3.7 Hz, C^5, **22b**), 128.8 (d, *J* = 14.8 Hz, C^1, **22b**), 130.1 (s, C^6, **22b**), 130.9 (d, *J* = 9.7 Hz, C^{2,6}, **22a**), 136.9 (d, *J* = 8.5 Hz, C^4, **22b**), 137.3 (d, *J* = 3.0 Hz, C^1, **22a**), 160.0 (d, *J* = 255 Hz, C^2, **22b**), 166.2 (d, *J* = 255 Hz, C^4, **22a**) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −34.1 (**22b**), −27.9 (**22a**) ppm.

2-Chlorophenyl Methyl Sulfone (24a) and 4-Chlorophenyl Methyl Sulfone (24b):[6c,19] GC: 2 peaks, t_R = 4.76 (**24b**) and 4.85 (**24a**) min (ratio **24a/24b** = 74:26). MS (EI): *m/z* (%) of **24a** = 192 (22) [M$^{+\cdot}$], 190 (57) [M$^{+\cdot}$], 177 (14), 175 (36), 130 (20), 129 (18), 128 (65), 127 (40), 113 (34), 111 (100), 99 (25), 76 (14), 75 (74), 74 (25), 73 (11), 51 (17), 50 (46). MS (EI): *m/z* (%) of **24b** = 192 (17) [M$^{+\cdot}$], 190 (45) [M$^{+\cdot}$], 177 (16), 175 (44), 128 (35), 127 (34), 113 (34), 111 (100), 99 (17), 75 (60). ^{1}H NMR of the mixture of **24a** and **24b** (400 MHz, $CDCl_3$): δ = 3.01 (s, SO_2Me, **24b**), 3.23 (s, SO_2Me, **24a**), 7.42−7.47 (ddd, *J* = 7.8, 6.5, 2.2 Hz, C^{5}H, **24a**), 7.49−7.60 (m, C^{3,4}H of **24a** and C^{3,5}H of **24b**), 7.83−7.87 (m, C^{2,6}H, **24b**), 8.11 (ddd, *J* = 7.8, 1.3, 0.6 Hz, C^{6}H, **24a**) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.8 (C−SO_2*Me*, **24a**), 44.5 (C−SO_2*Me*, **24b**), 127.7 (CH phenyl of **24a**), 129.0 and 129.7 (CH phenyl of **24b**), 130.8 and 131.9 (CH phenyl of **24a**), 132.4 (C−Cl or *C*−SO_2Me of **24a**), 134.9 (CH phenyl of **24a**), 137.9 (C−Cl or *C*−SO_2Me of **24a**), 139.0 and 140.3 (C−Cl or *C*−SO_2Me of **24b**) ppm.

2,3-Dichlorophenyl Methyl Sulfone (25a) and 3,4-Dichlorophenyl Methyl Sulfone (25b): GC: 2 peaks, t_R = 5.79 (**25b**) and 5.94 (**25a**) min. MS (EI): *m*/*z* (%) of **25a** = 226 (46) [$M^{+\cdot}$], 224 (M+., 64), 211 (22), 209 (33), 165 (14), 164 (51), 163 (29), 162 (80), 161 (37), 147 (64), 145 (100), 111 (24), 109 (65), 75 (50), 74 (61), 63 (20), 50 (13). MS (EI): *m*/*z* (%) of **25b** = 226 (36) [$M^{+\cdot}$], 224 (52) [$M^{+\cdot}$], 211 (34), 209 (50), 165 (10), 164 (23), 163 (31), 162 (37), 161 (45), 147 (65), 145 (100), 111 (20), 109 (58), 75 (41), 74 (47), 63 (14), 50 (11). ^{1}H NMR of the mixture of **25a** and **25b** (400 MHz, $CDCl_3$): δ = 3.04 (s, SO_2Me, **25b**), 3.26 (s, SO_2Me, **25a**), 7.40 (t, *J* = 8 Hz, C^5H, **25a**), 7.64 (d, *J* = 8.4 Hz, C^5H, **25b**), 7.70−7.77 (m, *J* = 8.4, 2 Hz, C^4H of **25a** and C^6H of **25b**), 8.0 (d, *J* = 2 Hz, C^2H, **25b**), 8.07 (dd, *J* = 8, 2 Hz, C^6H, **25a**) ppm; ratio **25a**/**25b** estimated by ^{1}H NMR = 4:96. ^{13}C NMR of **25b** (50 MHz, $CDCl_3$): δ = 44.5 (C−SO_2*Me*), 126.6, 129.6, 131.6 ($C^{2,5,6}H$), 134.2, 138.9 and 140.2 ($C^{1,3,4}$) ppm.

2,4-Difluorophenyl Methyl Sulfone (26): GC: t_R = 3.51 min. MS (EI): *m*/*z* (%) = 192 (46) [M^+], 177 (56), 130 (44), 129 (100), 113 (70), 101 (25), 63 (56). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.12 (s, 3 H, SO_2Me), 6.90−7.10 (m, 2 H, $C^{3,5}H$), 7.80−7.95 (m, 1 H, C^6H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.9 (d, *J* = 1.5 Hz, SO_2Me), 105.8 (t, *J* = 25.6 Hz, C^3H), 112.3 (dd, *J* = 22, 3.8 Hz, C^5H), 125.0 (dd, *J* = 15 and 4 Hz, C^1), 131.8 (dd, *J* = 10.5, 1.2 Hz, C^6H), 160.4 (dd, *J* = 259, 11.7 Hz, $C^{2\text{ or }4}$−F), 166.5 (dd, *J* = 257, 13 Hz, $C^{2\text{ or }4}$−F) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −29.4, −23.4 ppm.

4-Fluoro-3-methylphenyl Methyl Sulfone (27a), 3-Fluoro-2-methylphenyl Methyl Sulfone (27b), 3-Fluoro-4-methylphenyl Methyl Sulfone (27c), 2-Fluoro-3-methylphenyl Methyl Sulfone (27d): GC: t_R = 4.24 (**27c**), 4.35 (**27a**), 4.39 (not assigned), and 4.56 (not assigned) min in the respective proportions 6:66:16:12; For **27a**: MS (EI): *m*/*z* (%) of **27a** = 188 (50) [M^+], 173 (42), 125 (33), 109 (100), 83 (30). ^{1}H NMR of the mixture (400 MHz, $CDCl_3$): δ = 2.30−2.33 (m, C−*Me*, **27a**, **27b**, **27d**), 2.57 (d, *J* = 2.5 Hz, C−*Me*, **27c**), 2.99 (s, SO_2Me, **27a**, **27b** or **27d**), 3.00 (s, SO_2Me, **27a**, **27b** or **27d**), 3.05 (s, SO_2Me, **27c**), 3.17 (s, SO_2Me, **27a**, **27b** or **27d**), 7.13 (t, 1 H, C^5H, **27a**), 7.17−7.20 (m, not assigned), 7.25−7.38 (m, not assigned), 7.42−7.47 (m, not assigned), 7.51−7.60 (m, not assigned), 7.70−7.74 (m, C^6H, **27a**), 7.74−7.78 (m, C^2H, **27a**), 7.79−7.85 (m, not assigned) ppm. ^{13}C NMR of **27a** (50 MHz, $CDCl_3$): δ = 15.0 (d, *J* = 3.5 Hz, C−*Me*), 44.8 (C−SO_2*Me*), 116.3 (d, *J* = 23.9 Hz, C^5), 127.0 (d, *J* = 18.5 Hz, C^3), 127.6 (d, *J* = 9.8 Hz, C^6), 131.3 (d, *J* = 6.7 Hz, C^2), 136.3 (d, *J* = 3.5 Hz, C^1), 164.5 (d, *J* = 255 Hz, C^4) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −28.9 (**27a**), −33.6, −34.3, −35.2 ppm.

2-Methyl-4-fluorophenyl Methyl Sulfone (28a), 2-Fluoro-4-methylphenyl Methyl Sulfone (28b), 2-Fluoro-6-methylphenyl Methyl Sulfone (28c): GC: t_R = 4.08 (**28a**), 4.19 (**28c**) min and 4.45 (**28b**) min in the respective proportions 62:12:26; For the peak at 4.08 min. MS (EI): *m*/*z* (%) of **28a** = 188 (58) [$M^{+\cdot}$], 173 (42), 125 (35), 109 (100), 107 (19), 83 (36), 57 (10). MS (EI): *m*/*z* (%) of **28c** = 188 (94) [$M^{+\cdot}$], 173 (34), 125 (100), 109 (84), 107 (35), 83 (46), 57 (24); For the peak at 4.45 min. MS (EI): *m*/*z* (%) of **28b** = 188 (56) [$M^{+\cdot}$], 173 (63), 125 (100), 109 (65), 107 (13), 83 (36), 57 (16). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, C−*Me*, **28b**), 2.61 (s, C−*Me*, **28a** and **28c**), 3.00 (s, SO_2Me, **28a**), 3.10 (s, SO_2Me, **28b**), 3.16 (d, *J* = 2 Hz, SO_2Me, **28c**), 6.93−7.08 (m, not assigned), 7.37 (td, *J* = 8 and 5.5 Hz, C^4H, **28c**), 7.69 (t, *J* = 7.7 Hz, C^6H, **28b**), 7.94 (dd, *J* = 9.5, 5.5 Hz, C^6H, **28a**) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.8 (s, C−*Me*, **28a**), 20.9 (s, C−*Me*, **28c**), 21.4 (s, C−*Me*, **28b**), 43.6 (s, C−SO_2*Me*, **28a**), 43.7 (d, *J* = 2.8 Hz, C−SO_2*Me*, **28b**), 45.3 (d, *J* = 5.9 Hz, C−SO_2*Me*, **28c**), 113.5 (d, *J* = 21.9 Hz, C^5, **28a**), 114.8 (d, *J* = 23.9 Hz, C^3, **28c**), 117.4 (d, *J* = 20.9 Hz, C^3, **28b**), 119.3 (d, *J* = 22.2 Hz, C^3, **28a**), 125.2 (d, *J* = 14.8 Hz, C^1, **28b**), 125.3 (d, *J* = 3.1 Hz, C^5, **28b**), 127.0 (d, *J* = 12.6 Hz, C^1, **28c**), 128.8 (d, *J* = 3 Hz, C^5, **28c**), 129.2 (s, C^6, **28b**), 132.0 (d, *J* = 9.9 Hz, C^6, **28a**), 134.4 (d, *J* = 10.4 Hz, C^4, **28c**), 134.7 (d, *J* = 3 Hz, C^1, **28a**), 140.7 (s, C^6, **28c**), 141.0 (d, *J* = 9.3 Hz, C^2, **28a**), 148.0 (d, *J* = 8.4 Hz, C^4, **28b**), 159.1 (d, *J* = 254 Hz, C^2, **28b**), 160.2 (d, *J* = 253 Hz, C^5, **28c**), 165.1 (d, *J* = 255 Hz, C^5, **28a**) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −29.5 (**28a**), −31.1 (**28c**) and −35.5 (**28b**) ppm.

2-Fluoro-5-methylphenyl Methyl Sulfone (29a), 2-Methyl-5-fluorophenyl Methyl Sulfone (29b): GC: t_R = 4.23 (not assigned), and 4.50 (not assigned) min in the respective proportions 48:52; For the peak at 4.23 min. MS (EI): *m*/*z* (%) = 188 (100) [$M^{+\cdot}$], 173 (19), 125 (33), 125 (54), 109 (83), 108 (79), 107 (32), 83 (43); For the peak at 4.50 min. MS (EI): *m*/*z* (%) = 188 (64) [M^+], 173 (36), 126 (44), 125 (37), 109 (100), 107 (19), 97 (18), 63 (28), 57 (31). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, C−*Me*, **29a**), 2.63 (s, C−*Me*, **29b**), 3.05 and 3.16 (s, SO_2Me, **29a**,or **29b**), 7.09 (dd, *J* = 8.5, 9.7 Hz, C^3H, **29a**), 7.18 (td, *J* = 2.8, 7.9 Hz, C^4H, **29b**), 7.29 (dd, *J* = 5.2, 8.5 Hz, C^3H, **29b**), 7.38 (m, C^4H, **29a**), 7.60−7.80 (m, C^6H of **29a** and C^6H of **29b**) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.6 (s, C−*Me*, **29b**), 20.7 (s, C−*Me*, **29a**), 43.6 (s, C−SO_2*Me*, **29a** or **29b**), and 44.0 (d, C−SO_2*Me*, **29a** or **29b**), 116.5, 116.7, 116.9 and 117.1 (C^3H of **29a** and C^2H of **29b**), 120.8 (d, *J* = 21 Hz, C^4H, **29b**), 128.0 (d, *J* = 18.5 Hz, C^1, **29a**), 129.7 (C^6, **29a**), 133.3 (d, *J* = 3.6 Hz, C^2, **29b**), 134.6 (d, *J* = 7 Hz, C^5H, **29b**), 135.0 (d, *J* = 3.9 Hz, C^5H, **29a**), 136.6 (d, *J* = 8 Hz, C^4H, **29a**), 140.2 (C^1, **29b**), 157.7 (d, *J* = 252 Hz, C^2, **29a**), 160.8 (d, *J* = 250 Hz, C^5, **29b**) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −35.0 and −36.3 (**29a** and **29b**) ppm.

Acknowledgments

Thanks are due to the Centre National de la Recherche Scientifique and Rhodia Organique Fine for financial support. Professor Ram Mohan is gratefully acknowledged for his kind contribution to the preparation of the manuscript.

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[7] Typical procedure: Compound **2** (630 mg, 2 mmol), toluene (**4**, 5.53 g, 60 mmol), methanesulfonyl chloride (2.29 g, 20 mmol) and **1** (0.3 g, 2 mmol) were placed successively in a 50 mL flask. The flask was fitted with a condenser connected to an argon line, immersed in an oil bath, and heated for 36 h at 110 °C. After the system had cooled, dichloromethane (20 mL) and aqueous HCl (6%, 20 mL) were added. The products were extracted with dichloromethane (2 × 20 mL). The combined organic phases were dried with $MgSO_4$ and concentrated. The crude mixture was subjected to flash chromatography on silica gel (eluent: CH_2Cl_2/pentane, 1:1) to give the tolylmethylsulfones (**17**, 3.13 g, 92% isolated yield). All products **17**−**29** were identified by comparison with authentic samples prepared by known procedures[6b,6c,8] and their isomer compositions were determined by GC analysis.

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[14] The synthesis of **30** by use of a stoichiometric reaction between an alkanesulfonyl bromide and silver triflate has been reported by Effenberger et al.: K. Huthmacher, G. König, F. Effenberger, *Chem. Ber.* **1975**, *108*, 2947.

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[17] The amounts of **18** in complexation with **2** or **3** were estimated from stoichiometric mixtures of **2** or **3** and **18** in toluene (c = 86 mM) and were found to be 58 and 30%, respectively. For solubility reasons the same experiment could not be run with $BiCl(OTf)_2$ or $SbCl_2OTf$. In the case of $FeCl_3$ the amount of complexed sulfone is nearly quantitative, which explains the need for stoichiometric amounts of $FeCl_3$ for these reactions.[8a]

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Received May 24, 2004

