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## Bismuth(III) halides: remarkable doping agents for triflic acid in the catalytic sulfonylation of arenes

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## Abstract

The catalytic activity of triflic acid has been dramatically increased by the addition of a catalytic amount of bismuth(III) chloride. Thus, the catalytic sulfonylation of arenes using the new system BiCl<sub>3</sub>-triflic acid has been successfully carried out while both components of this catalytic system are poorly active or inactive alone, which suggests a synergy between BiCl<sub>3</sub> and triflic acid. Other bismuth halide-triflic acid systems proved to be active. © 1999 Elsevier Science Ltd. All rights reserved.

Sulfones are of great use in organic synthesis<sup>1</sup> as well as for industrial applications.<sup>2</sup> Some metal halides (FeCl<sub>3</sub><sup>1a,3</sup>), zeolithes,<sup>4</sup> or Brönsted acids (polyphosphoric acid<sup>5</sup>) have been reported to catalyze the sulfonylation of arenes. While triflic acid (TfOH) efficiently catalyses the Friedel–Crafts acylation of aromatics,<sup>6</sup> it poorly catalyses the sulfonylation of arenes.<sup>7</sup> Recently, we have reported that Bi(OTf)<sub>3</sub> was an efficient catalyst for this reaction.<sup>8</sup> The present paper reports our preliminary results on the catalysis of the sulfonylation of aromatics by the system BiCl<sub>3</sub>–TfOH (see Eq. 1 and Table 1).

ArH + Ar'SO<sub>2</sub>Cl \_\_\_\_\_BiCl<sub>3</sub> (5 %mol) + TfOH (10 %mol) ArSO<sub>2</sub>Ar' + HCl (1)

As can be seen from Table 1, the simple addition of a catalytic amount of  $BiCl_3$  to TfOH leads to high yields of sulfone in all the cases studied. Moreover,  $BiCl_3$  as well as triffic acid when used alone are poor catalysts of this reaction (for example see Table 1, entries 2 and 3, for the very reactive anisole). In addition, the  $BiF_3$ -TfOH,  $BiBr_3$ -TfOH and  $BiI_3$ -TfOH systems also proved to be active.

A typical experimental procedure is described for the benzenesulfonylation of mesitylene: In a 50 mL flask equipped with a condenser are successively introduced under argon, BiCl<sub>3</sub> (197 mg, 0.625 mmol), mesitylene (3 g, 24.96 mmol), benzenesulfonyl chloride (2.2 g, 12.48 mmol) and triflic acid (187 mg, 1.25 mmol). The mixture is heated at 120°C for 1 h. After cooling, 20 mL of a saturated aqueous NaHCO<sub>3</sub> solution are added and the products are extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×20 mL). After drying, evaporation

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Entry	ArH <sup>a</sup>	Ar'SO <sub>2</sub> Cl	Conditions	Catalyst <sup>c</sup>	Yield % <sup>d</sup>
			T °C <sup>b</sup> , (time, h)		[o:m:p]
1	anisole	PhSO <sub>2</sub> Cl	120, (0.5)	A	82 [47:0:53] <sup>e</sup>
2		"	н	В	trace
3	"	н	"	С	4
4	mesitylene	"	120, (1)	Α	95 <sup>f</sup>
5	"	н	**	В	8
6	<i>m</i> -xylene	11	11	Α	93 <sup>g</sup>
7	"	11		В	14
8	toluene	"	120, (1.25)	Α	95 [39:6:55] <sup>h</sup>
9	"	"	**	В	trace
10	benzene	19	80, (12)	Α	65 <sup>i</sup>
11		"	"	В	7
12	chlorobenzene	ч	120, (4)	А	70 [3:0:97] <sup>j</sup>
13	н	"	11	В	28 [3:0:97]
14	toluene	4-Me-C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl	120, (1.25)	А	97 [29:5:66] <sup>k</sup>
15	**	"	41	В	25 [29:5:66]
16	"	4-Cl-C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl	••	Α	95 [42:7:51] <sup>1</sup>
17	"		"	В	4 [42:7:51]

 Table 1

 Sulfonylation of arenes catalyzed by the system BiCl<sub>3</sub>-TfOH

<sup>a</sup> ArH/Ar'SO<sub>2</sub>Cl = 2/1; <sup>b</sup> temperature of the oil bath; <sup>c</sup> catalyst : A: BiCl<sub>3</sub> (5 %mol) + TfOH (10 %mol), B: TfOH (10 %mol), C: BiCl<sub>3</sub> (5 %mol); <sup>d</sup> by GC using tetradecane as internal standard; <sup>e</sup> (methoxyphenyl)-phenyl sulfone, accompanied by 15 % of phenyl benzenesulfonate; <sup>f</sup> (2,4,6-trimethylphenyl)-phenyl sulfone; <sup>g</sup> (2,4-dimethylphenyl)-phenyl sulfone, accompanied by 3 % of (2,6-dimethylphenyl)-phenyl sulfone; <sup>h</sup>phenyl tolyl sulfone; <sup>i</sup> diphenyl sulfone; <sup>j</sup> (chlorophenyl)-phenyl sulfone; <sup>k</sup> ditolyl sulfone; <sup>i</sup> (4-chlorophenyl)-tolyl sulfone.

of the organic phase and recrystallization of the solid product in ethanol, 2.82 g (87% yield) of (2,4,6-

trimethylphenyl)phenyl sulfone are obtained (Mp 81°C; litt.:<sup>9</sup> 80°C).

Finally, a mechanistic investigation of the activation of the catalytic power of triflic acid, the comparison of the activity of these Bi-based systems and their use for other reactions are currently underway.

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