



## FeCl<sub>3</sub> as an efficient and new catalyst for the thia-Fries rearrangement of aryl sulfinates

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**Abstract**—Aryl arenesulfinates rearrange to the corresponding arenesulfinyl phenols via a thia-Fries rearrangement on catalysis by anhydrous FeCl<sub>3</sub> in dry dichloromethane at room temperature in good to excellent yields. © 2001 Published by Elsevier Science Ltd.

Phenols are one of the most important classes of organic compounds because of their industrial applications and natural occurrence.<sup>1</sup> Chemical modifications of these compounds to prepare new derivatives has, therefore, attracted a great deal of attention. Phenols are highly reactive toward aromatic electrophilic substitutions and different ester derivatives such as carboxylates, sulfonates and sulfinates, have the ability to participate in reactions classified as Fries rearrangements.

The Fries rearrangements of carboxylates has been studied widely<sup>2</sup> and the search for new conditions is continuing,<sup>3</sup> whereas the rearrangement of sulfonate esters has received less attention.<sup>4</sup> In the case of sulfinate esters, a literature survey revealed that their Fries rearrangement has been reported only once in recent years.<sup>5</sup>

In continuing our research into microwave promoted rearrangements of different derivatives of phenols, such as propargyl ethers,<sup>6</sup> carboxylates<sup>2</sup> and especially sulfonate esters,<sup>4</sup> we became interested in the possibility of carrying out thia-Fries rearrangements of aryl sulfinate esters. However, when sulfinate esters were subjected to conditions used for sulfonates (sorption on ZnCl<sub>2</sub>, AlCl<sub>3</sub>/SiO<sub>2</sub> and microwave irradiation),<sup>4</sup> it was found that the sulfinates decomposed into complex mixtures and the rearrangement products were not formed.

Decomposition of sulfinate esters take place because of their thermal instability as indicated by the instability

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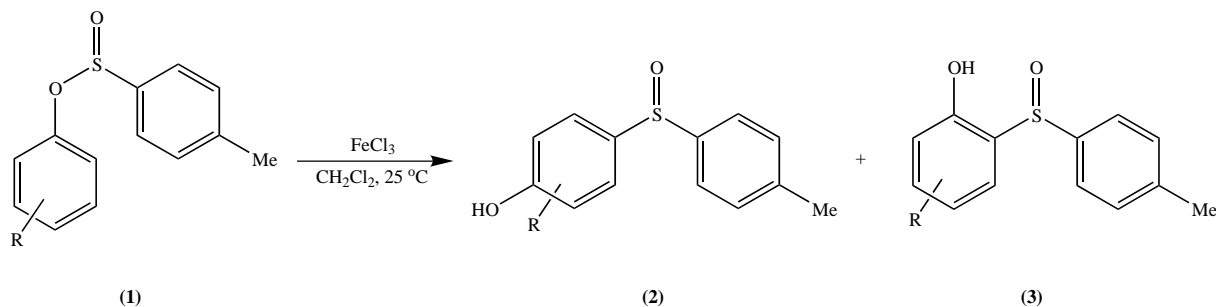
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of analogous acid chlorides and sulfinic acids.<sup>7</sup> Our supported reagent has only mild reactivity and it must be irradiated by microwaves leading to an increase of the reaction temperature and decomposition of the substrate before rearrangement. Although, a literature survey showed that alkyl sulfinate esters have been studied more than aryl ones, the former compounds suffer from thermal instability as well. The preparation of the latter compounds has been reported together with their rearrangement.<sup>5</sup> It has been shown that chiral alkyl sulfinates are most often employed as intermediates for the preparation of optically active sulfoxides and hence different methods have been developed for their preparation.<sup>7a-c,8</sup> A protocol involving a sulfinyl chloride and a phenol in the presence of a base works well for the preparation of aryl sulfinates at low temperatures.<sup>9</sup>

**Table 1.** Results of the rearrangement of *p*-methylphenyl *p*-toluenesulfinate with different Lewis acids in dry dichloromethane

Entry	Catalyst	Time (h)		Yield (%)
		Rt stirring	Refluxing	
1	TiCl <sub>4</sub>	24		7
2	SnCl <sub>4</sub>	24		17
3	ZrCl <sub>4</sub>	90	72	10
4	ZnCl <sub>2</sub>	24		15
5	FeCl <sub>3</sub>	1		75
6	AlCl <sub>3</sub>	2	2	45
7 <sup>a</sup>	AlCl <sub>3</sub> , ZnCl <sub>2</sub> /SiO <sub>2</sub>	10 (min)		0.0

<sup>a</sup> The sulfinate ester was absorbed on supported reagent and subjected to microwave irradiation.



**Scheme 1.** (a) R = H; (b) R = 4-Me; (c) R = 4-*t*Bu; (d) R = 2,6-dimethyl; (e) R = 4-Cl; (f) R = 4-Br; (g) R = 4-OMe.

**Table 2.** Thia-Fries rearrangement of aryl *p*-toluenesulfonates under optimized conditions

Entry	Sulfonate ester	Time (h)	Product <sup>a</sup>	Yield <sup>b</sup> (%)	OH (ppm)
	Aryl				
1	Phenyl	2	<b>2a</b>	82	7.6
2	4-Methylphenyl	1	<b>3b</b>	75	9.4
3	4- <i>tert</i> -Butylphenyl	1	<b>3c</b>	96	9.0
4	2,6-Dimethylphenyl	1	<b>2d</b>	73	7.6–7.2
5	4-Chlorophenyl	2	<b>3e</b>	72	10.1
6	4-Bromophenyl	2	<b>3f</b>	80	7.5
7	4-Methoxyphenyl	1	<b>3g</b>	100 <sup>c</sup>	

<sup>a</sup> The substrate conversion is quantitative.

<sup>b</sup> All yields refer to isolated compounds.

<sup>c</sup> The rearrangement product was isolated as a ferric complex and the given yield is based on the sulfonate ester conversion.<sup>11</sup>

As there was only one report in the literature on the thia-Fries rearrangement of aryl sulfinate esters, we decided to investigate the use of other Lewis acids. The first report described the application of AlCl<sub>3</sub> in dry dichloromethane for 1 h. We, therefore, examined different Lewis acids such as TiCl<sub>4</sub>, SnCl<sub>4</sub>, ZrCl<sub>4</sub>, ZnCl<sub>2</sub> and FeCl<sub>3</sub> with *p*-methylphenyl *p*-toluenesulfinate (**1b**, R = Me) as a model compound (Table 1). After performing several optimization experiments, it was found that FeCl<sub>3</sub> is the catalyst of choice and that the ratio of the catalyst to substrate was optimized at 2:1 (equiv./equiv.). Rearrangement proceeded in dry dichloromethane under an inert atmosphere at room temperature and the reaction was monitored by TLC<sup>10</sup> (Scheme 1).

Different aryl sulfinate esters were studied under the optimized conditions and Table 2 summarizes the results. Substrates with electron donating groups are more reactive than those with electron withdrawing groups (Table 2, entries 2, 3, 4, 7). Rearrangement products involve *ortho* and *para* migration of the sulfinyl group and the *para*-product predominates. For instance, with phenyl *p*-toluenesulfinate (**1a**, R = H), the main product was the *para*-isomer (82%) and only a trace amount of the *ortho*-isomer was formed. The structures of the reaction products were established by NMR spectroscopy. Participation of the phenolic hydroxyl group in intramolecular hydrogen bonding in the *ortho*-isomers led to hydroxyl resonances at lower field compared to the corresponding proton in the *para*-isomer (Table 2).

In conclusion, a novel method for the thia-Fries rearrangement of sulfinate esters has been developed in our laboratory. The mild catalyst is less corrosive than the previously reported AlCl<sub>3</sub>. Diverse substrates have led to high yields of the rearranged products.

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9. The sulfinat esters were prepared (Refs. 5, 8g,h) as follows: Sulfinyl chloride was prepared in situ from powdered and dried sodium *p*-toluenesulfinate (1 g, 5.62 mmol) added in one batch to a solution of thionyl chloride (2 ml, 28 mmol) in dry benzene (5 ml) at 0°C. After the completion of the reaction, the excess thionyl chloride and benzene were evaporated until a green gel remained. Dry ether (5 ml) was added to the gel and a white precipitate (NaCl) appeared, the mixture was cooled to -20°C. Pyridine (1 ml) and phenol (5.62 mmol) were added and a white precipitate was formed. The mixture was stirred for 8 h at -20°C, then diluted with ether and water, and subsequently treated with 5% aq. citric acid, saturated NaHCO<sub>3</sub>, 0.25N NaOH and brine and the organic phase was dried using MgSO<sub>4</sub>. Evaporation of the solvent gave the aryl *p*-toluenesulfinate in good yields. The esters obtained have low mps and must be used immediately or kept in a refrigerator [IR: 1135 cm<sup>-1</sup> (S=O); 835 cm<sup>-1</sup> (S-O)].
10. General procedure for the thia-Fries rearrangement of aryl sulfinat esters: 1.5 mmol of the ester and 3 mmol FeCl<sub>3</sub> in (8 ml) dry dichloromethane was used under nitrogen. FeCl<sub>3</sub> was added in one batch and a change in color was observed immediately. The reaction mixture was stirred for the required time (see Table 2) at 25°C. The reaction was diluted with dichloromethane and water, then 5 ml conc. HCl was added to the reaction mixture suspended in crushed ice and usually accompanied with a change in color of the organic phase. The organic phase was washed with water and brine and dried over MgSO<sub>4</sub>. The crude product, after evaporation of the solvent, was crystallized from ethanol and hexane or purified by column chromatography on silica gel (eluent: dichloromethane, petroleum ether). Spectral data for selected compounds: [2-(4-methylphenyl) sulfinyl-4-*tert*-butyl phenol (**3c**): mp=140°C; IR (KBr pellet) cm<sup>-1</sup>: 3192 (OH, intramolecular hydrogen bonding), 2951, 1015 (S=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.0 (bs, 1H, OH), 7.9–7.6, 7.1–6.8 (4H, AA'BB' system), 7.6–7.3 (m, 3H, aromatic), 2.5 (s, 3H, Me), 1.4 (s, 9H, *t*-Bu); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 167, 158, 143, 142, 140, 130, 125, 123, 122, 119, 34, 31, 21.; [2-(4-methylphenyl)sulfinyl-4-chloro phenol(**3b**): mp=169°C, IR (KBr pellet) cm<sup>-1</sup>: 3061 (OH, intramolecular hydrogen bonding), 1000 (S=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.1 (bs, 1H, OH), 7.6–7.3, 6.8–6.5 (4H, AA'BB' system), 7.2–6.9 (m, 3H, aromatic), 2.2 (s, 3H, Me); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 168, 147, 146, 138, 136, 135, 130, 129, 127, 123, 26.
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