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Thia-Fries rearrangement of aryl sulfonates in dry media under microwave activation

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Abstract

An $AlCl_3$–$ZnCl_2$ mixture supported on silica gel is found to be a new efficient medium for the thia-Fries rearrangement of aryl sulfonates in solvent-free conditions under microwave dielectric heating. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: thia-Fries rearrangement; aryl sulfonates; microwave irradiation; dry media.

Fries rearrangements of sulfonate esters have received little attention, despite their potential utility to produce useful organosulfur compounds such as drug and agrochemical intermediates,[1] thermographic materials[2] and effective antiviral agents.[3] However, these rearrangements require drastic reaction conditions (neat with more than stoichiometric amounts of $AlCl_3$ at 80–160°C or in refluxing nitrobenzene) and produce very low yields (generally <20%) of the desired products.[4] Supported clays as Lewis acids give better results but still the temperatures are relatively high (140°C) and several hours are required for the reaction to go to completion. The method has not been applied to a wide range of aryl sulfonates.[5]

The coupling of microwave irradiation with the use of catalysts or mineral supported reagents, under solvent-free conditions, provides chemical processes with special attributes such as enhanced reaction rates, higher yields, greater selectivity and improved ease of manipulation.[6] Recently, we found that an $AlCl_3$–$ZnCl_2$ mixture supported on silica gel is an efficient medium for the promotion of the Fries rearrangement of acyloxy benzenes and naphthalenes under microwave irradiation.[7] In the continuation of our study of microwave assisted reactions,[8] we now report the efficiency of this medium for promoting the thia-Fries rearrangement of aryl sulfonates under environmentally benign conditions under microwave irradiation.

When neat *p*-methylphenyl *p*-toluenesulfonate was mixed with the support (1:3 w/w)[9] and subjected to microwave irradiation[10] for 8 min, after conventional work-up, a 92% yield of the *ortho*-directed product (2-hydroxy-5-methyl *p*-tolyl sulfone) (Table 1, entry 2) was obtained. Several further examples have been investigated and Table 1 summarizes our results, along with the melting points and chemical shifts of the

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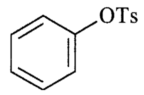
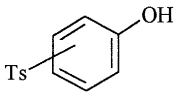
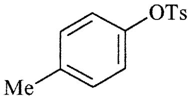
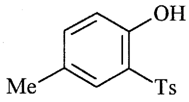
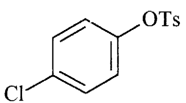
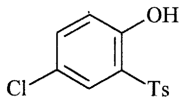
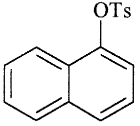
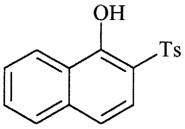
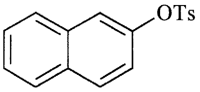
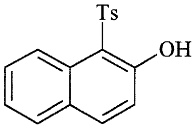
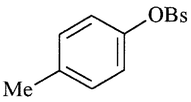
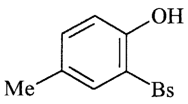
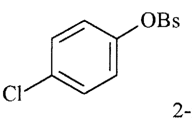
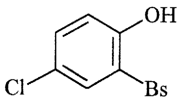
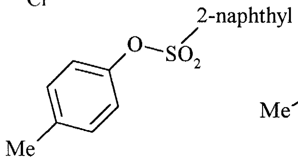
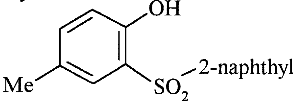
intramolecular hydrogen-bonded hydroxyl groups in the products. In most cases, a single product derived from the *ortho*-shift of the sulfonyl group was obtained (Table 1). Phenyl *p*-toluenesulfonate gave an 87% yield of products (80% *ortho* and 20% *para*) after 10 min irradiation (Table 1, entry 1). When phenyl *p*-toluenesulfonate is heated to 120°C with 3 equivalents of $AlCl_3$ for about 2 h, a 12% yield of isomeric hydroxyphenyl *p*-tolyl sulfones was obtained.[11] Clearly, the reaction time in our work has been reduced almost 12 times and the yield is much higher (87% versus 12%).

Table 1
Thia-Fries rearrangement of aryl sulfonates

Entry	Substrate[a]	Product[b]	Time / min.[c] (%Yield)[d]	m.p. (°C) found (lit.)	δ OH(ppm)
1			10 (87)	126 (126-7)[12a] *(ortho)* 143 (142-3)[12a] *(para)*	9.15 6.5-8.3
2			8 (92)	135 (130-2)[12a]	9.0
3			10 (81)	127 (125-6)[12a]	9.15
4			7 (78)	134 (133-4)[12b]	10.5
5			10 (67)	129 (129-30)[12c]	11.0
6			10 (74)	184-6 (-)	8.8
7			10 (69)	160 (-)	9.0
8			10 (80)	160 (159-60)[12c]	9.25

a)- The starting materials were prepared by modified literature procedures.[11]
b)- All products were characterized by m.p., IR, ^1H NMR, and their spectroscopic data were similar to those reported in the litrature.[12]
c)- The reaction times were optimized after several experiments.
d)- All yields refer to isolated products.

With more bulky naphthyl sulfonates the rearrangement is also regiospecific and the 2-isomers are the exclusive products (Table 1, entries 4 and 5). This is in accordance with our recent results of *ortho*-directed rearrangement of acyloxy benzenes and naphthalenes.[7] 4-Nitrophenyl *p*-toluenesulfonate does not rearrange to the corresponding sulfone but hydrolysis of the sulfonate ester takes place in 40% yield. This result indicates that electrophilic substitution does not occur, because the electron-withdrawing group (4-nitro) deactivates the aromatic ring.

To demonstrate the efficiency of the methodology, when *p*-methylphenyl *p*-toluenesulfonate (Table 1, entry 2) was mixed with the support, heated to about 250°C (the reaction mixture reaches this temperature in microwave oven after 10 min) for 10 min in an oil bath, only the unchanged starting material was isolated from the reaction medium. Furthermore, when the reaction mixture was heated at 250°C for a longer period, some reaction product along with a tarry material was obtained owing to decomposition of both product and starting material.

In conclusion, an $AlCl_3$–$ZnCl_2$ mixture supported on silica gel has been shown to be an efficient medium for a regiospecific thia-Fries rearrangement of aryl sulfonates under microwave irradiation. This method has the advantage of: (a) being a readily available medium; (b) the reaction is fast and solvent-free; (c) a wide range of aryl or naphthyl sulfonates are rearranged by this medium; and, finally (d) the ease of the work-up.

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9. The support was prepared as described in Ref. 7 and the minimum amount of supported reagent to substrate was found to be 3:1 (w/w) after performing several optimization experiments. General procedure for thia-Fries rearrangement of sulfonates: To a solution of arylsulfonate (1 g) in 5 ml of anhydrous chloroform, 3 g of support was added. After evaporation of the solvent, the mixture was subjected to microwave irradiation for the given times (Table 1). The cooled reaction mixture was extracted with ethyl acetate (3×50 ml) and the solvent was evaporated under vacuum. The product was isolated by column chromatography of the crude reaction mixture on silica gel (eluent: dichloromethane:petroleum ether).
10. The microwave oven used for this work was an AEG (650 Watt) at 2450 MHz (100% power) which was modified to a focused monomode system in our laboratory.
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