SHORT PAPER

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Fries rearrangement of arylsulfonates and sulfonanilides under microwave irradiation†

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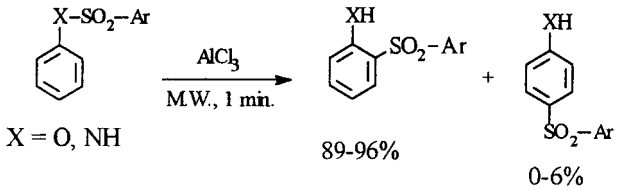
Fries rearrangements of arylsulfonates and sulfonanilides under microwave irradiation afforded hydroxy and aminoaryl sulfones respectively in very short times and in excellent yields. The conversion showed high selectivity to produce 2- and 4- hydroxyaryl sulfones as the major and minor products respectively from arylsulfonates and 2-aminoaryl sulfones exclusively from aryl sulfonanilides.

Hydroxy and aminoaryl sulfones are important precursors for the synthesis of various organosulfur compounds.[1] These sulfones can be prepared by Fries rearrangement of arylsulfonates and sulfonanilides and the rearrangement can be effected thermally[2] or photochemically.[2b,3] However, thermal rearrangement[2] requires high temperature and the yield of the products is low. Heating of phenyl toluene-*p*-sulfonate with anhydrous $AlCl_3$ in CS_2 at 140°C for 1.5 h yielded[2a,b] the rearranged products, 2- and 4- hydroxyphenyl *p*-tolylsulfones in about 40% yield. When the cation-exchanged montmorillonite clays were used as catalyst, instead of anhydrous $AlCl_3$ the yield of the rearranged products was found[1a] to be highly increased. However, the rearrangement requires higher temperature (180°C) for a longer period of time (2–12hr) and the preparation of catalysts requires special techniques. The photo-Fries rearrangement of arylsulfonates and sulfonanilides afforded[3] a mixture of products including phenols and aryl amines respectively and as a result, the yield of individual sulfones became low. Some authors have utilised[4] cyclodextrin encapsulation to change the yield of the products of the photo-Fries rearrangement of sulfonyl derivatives.

We have recently carried out the Fries rearrangement of arylsulfonates and sulfonanilides in the presence of anhydrous $AlCl_3$ under microwave irradiation to prepare hydroxy and aminoaryl sulfones respectively (Scheme 1, Table 1). The rearrangement has been found to occur in a very short time (1 min) and the yields of the products were very high. The experimental procedure is simple and there were no undesirable side products. The rearrangement occurred with high selectivity. 2- and 4-Hydroxyaryl sulfones were formed as the major and minor products respectively from arylsulfonates and 2-aminoaryl sulfones were formed exclusively from arylsulfonanilides (Table 1). The structures of all the products were established from their analytical and spectral data.



Scheme 1

In conclusion, we have developed a convenient and efficient method for the preparation of hydroxy and aminoaryl sulfones by Fries rearrangement of arylsulfonates and sulfonanilides respectively under microwave irradiation. The time required for the rearrangement is very short. The products are formed in excellent yields and with high selectivity. To our knowledge, this is the first report of Fries rearrangement of arylsulfonates and sulfonanilides under microwave irradiation to prepare hydroxy and aminoaryl sulfones respectively.

Experimental procedure

Phenyl toluene-*p*-sulfonate (124 mg, 0.5 mmol) was mixed thoroughly with anhydrous $AlCl_3$ (92 mg, 0.7 mmol). The mixture was kept inside a microwave oven (BPL BMO 700T, 466 watt) and irradiated for 1 min. The reaction mixture was then removed from the oven, cooled and added to water (10 ml). This was extracted with $CHCl_3$ (3×10 ml) and purified by column chromatography over silica gel using EtOAc as eluent to yield 2- and 4-hydroxyphenyl-*p*-tolylsulfones (112 mg, 90% and 7 mg, 6% respectively).

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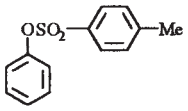
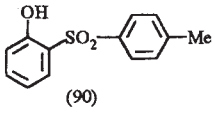
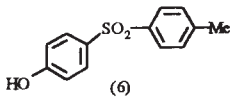
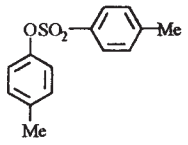
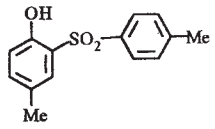
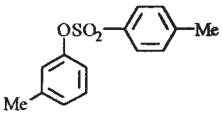
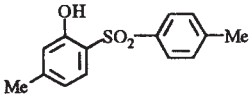
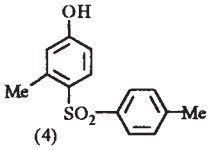
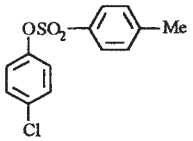
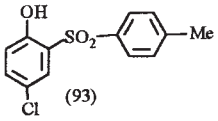
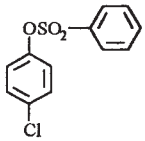
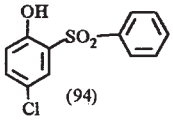
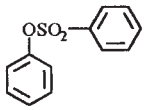
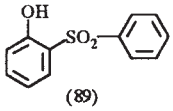
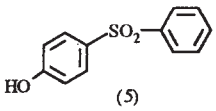
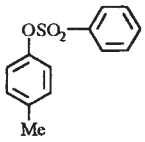
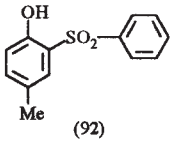
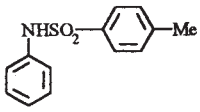
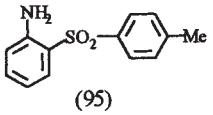
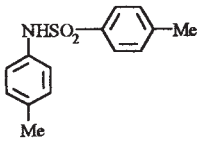
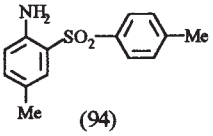
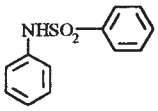
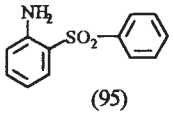
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Table 1 Fries rearrangement of arylsulfonates and sulfonanilides under microwave irradiation[a]

Entry	Arylsulfonate / sulfonanilide	2-Hydroxy/aminoarylsulfone (Isolated yield)	4-Hydroxy arylsulphone (Isolated yield)	Ref.
1.		 (90)	 (6)	2a,b
2.		 (96)		2a,b
3.		 (90)	 (4)	2a,c
4.		 (93)		2a
5.		 (94)		2b
6.		 (89)	 (5)	2b,4c
7.		 (92)		2b
8.		 (95)		5
9.		 (94)		6
10.		 (95)		4a

[a]All the products were characterised from their analytical data and spectral (IR, 1H NMR and MS) properties.