

Convenient Method for the Preparation of Aryl Sulfinyl Chlorides

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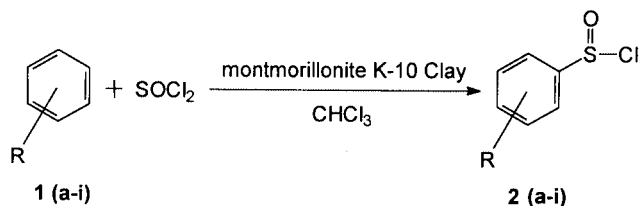
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Abstract: Reaction of activated arenes with thionyl chloride in the presence of montmorillonite K-10 clay affords the corresponding aryl sulfinyl chlorides in good yield.

Key words: sulfinylation, thionyl chloride, montmorillonite K-10 clay

Sulfinyl chlorides constitute the most valuable and versatile intermediates for the preparation of chiral sulfoxides, sulfonates and other natural products containing sulfur atom.¹ Despite their synthetic utility, the most practical methods available for their preparation include (1) reaction of sulfinic acid with thionyl chloride,^{2a} (2) treatment of thiol ester with thionyl chloride^{2b} and (3) reaction of disulfides with chlorine.^{2c,d} Although all of these methods afford the sulfinyl chlorides in good yields, they suffer from drawbacks such as use of hazardous reagent, over oxidation and incompatibility with other functional groups present. As only few sulfinic acids are commercially available, we looked for an alternative and simple procedure for direct sulfinylation of arenes. Direct preparation of arene sulfinyl chlorides from arenes remains little explored. We rationalised that reaction of thionyl chloride with arenes in the presence of trifluoro acetic acid³ to furnish the corresponding sulfoxide can be exploited to our advantage to provide the corresponding sulfinyl chlorides by judicious choice of the Lewis acid. Accordingly, arenes were treated with thionyl chloride in the presence of montmorillonite K-10 clay and as envisaged the reaction proceeds very smoothly to afford the respective sulfinyl chlorides (Scheme) in high yield.



Scheme

As is obvious from the Table our process provides good yields of various substituted sulfinyl chlorides. However, unactivated arenes suffered in terms of yield and reaction

time (entry **1j**). It is noteworthy that sulfinyl chlorides are obtained in virtually pure states as no by products are formed in the reaction.

Table Montmorillonite K-10 Clay Mediated Sulfinylation of Arenes.^a

Adduct	Arene (1)	Time (h)	Product (2)	Yield ^{b,c} (%)
a		6		61
b		4		82
c		2		84
d		3		68
e		6		72
f		2		91
g		2		87
h		2		76
i		2		89
j		14	No reaction	-

^a All the reactions were carried out in chloroform.

^b Yields are of isolated products.

^c All the products were identified by comparison of the physical and spectral data with those of literature.

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In conclusion, the present method proceeds under mild conditions using inexpensive thionyl chloride and eco-friendly montmorillonite K-10 clay.⁴ Further, the simplicity of the method coupled with use of easily available reagents should make it a method of choice for synthesizing various substituted aryl sulfinyl chlorides.

Sulfinyl Chlorides **2f**; General Procedure

To a well stirred solution of arene **1f** (9 mmol) and montmorillonite K-10 clay (1 g) in chloroform (10 mL) was introduced thionyl chloride (18 mmol) drop wise over a period of five minutes. After the gas evolution ceased, the reaction mixture was warmed to 50 °C and the progress of reaction was monitored by TLC. After completion of the reaction, the clay was filtered off and solvent was removed under vacuo to furnish the sulfinyl chloride **2f** (1.5 g, 91%).

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