

Note

Solid state oxidation of aromatic sulfides to corresponding phenyl and *p*-tolyl sulfoxides and sulfone using oxone®

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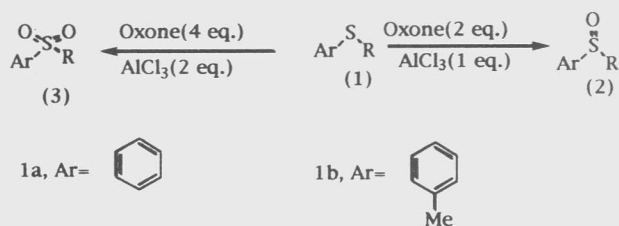
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Phenyl and *p*-tolyl sulfides **1** can be selectively oxidised to the corresponding sulfoxides **2** or sulfones **3** in solid state condition using oxone. The advantages of this method are the use of cheap and safe reagents, high yield and simple operating conditions.

Most organic reactions have been studied in solution. However, some organic reactions have been found to occur efficiently in the solid state¹. Solid state reactions are usually carried out by keeping a mixture of finely powdered reactant and reagent at room temperature. In some cases solid state reactions are accelerated by grinding of the reaction mixture using a mortar and pestle².

Sulfoxides and sulfones find wide application in organic synthesis, particularly in carbon-carbon bond forming process³. As part of our ongoing synthetic project we required an efficient method for the synthesis of a number of sulfoxides. These compounds are usually prepared by the oxidation of the corresponding sulfides **1**. Unfortunately these reagents in our hands gave mixture of the corresponding sulfoxide and the sulfone and also operating condition was difficult⁴.

More recently buffered Oxone® (potassium peroxymonosulfate) in acetone and aqueous KHCO₃ or K₂CO₃ has been reported by us as an effective and inexpensive substitute for *m*-CPBA for the oxidation of imines to the corresponding oxaziridines⁵. In our hands this procedure proved extremely sluggish for the oxidation of sulfides to the corresponding sulfoxides and sulfones. We found that by conducting these reactions in solid state the oxidation was extremely rapid (0.5 hr) and almost quantitative from ¹H NMR analysis. The general reaction is detailed in Scheme I and



Scheme I

the products are given in Table I. In all cases, the crude product was judged to be of 95% purity based on ¹H NMR and TLC analyses.

The reaction of **1** with two equivalents of oxidant gave only the sulfoxides **2** (Table I), while with four equivalents of oxidant under the same condition gave only the sulfones **3** (Table I) in high yields.

In conclusion, we report here an efficient, rapid and inexpensive method for the synthesis of aromatic sulfoxides and sulfones, which is superior to the previously reported methods in terms of yields and purity of the products.

Experimental Section

Preparation of sulfoxides **2**: General method.

A mixture of the appropriate sulfide (1.72 mmoles), oxone® (2.4 g, 3.96 mmoles) and AlCl₃ (0.22 g, 1.7 mmoles) was ground with agate pestle and mortar for 0.5 hr, and the product was taken up in dichloromethane (3 x 10 mL). The solution was washed with aqueous 20% NaHCO₃ and water, dried (MgSO₄) and the solvent evaporated. The product was >95% pure as found by TLC and ¹H NMR analyses. The product could be further purified by short path distillation or column chromatography.

Preparation of sulfones **3**: General method. A

mixture of the appropriate sulfide (1.72 mmoles), oxone® (4.8 g, 7.92 mmoles) and AlCl₃ (0.44 g, 3.4 mmoles) was ground with agate pestle and mortar for 0.5 hr, and the product was taken up in dichloromethane (3 x 10 mL). The solution was washed with aqueous 20% NaHCO₃ and water,

Table I—Yields of sulfoxides 2 and sulfones 3

Entry	Sulphides 1		Yield of 2 (%)	Yield of 3 (%)
	Ar	R*		
1	Ph	Me	96	96
2	Ph	Ph-CH ₂	98	97
3	Ph	Et	95	95
4	Ph	CH ₂ CO ₂ Me	97	98
5	Ph	CH ₂ CO ₂ <i>t</i> Bu	98	98
6	Ph	Ar'COCH ₂	96	97
7	Ph	Ph COCH ₂	97	96
8	4-CH ₃ -C ₆ H ₄	Me	96	96
9	4-CH ₃ -C ₆ H ₄	Ph-CH ₂	98	99
10	4-CH ₃ -C ₆ H ₄	Et	95	97
11	4-CH ₃ -C ₆ H ₄	CH ₂ CO ₂ Me	99	97
12	4-CH ₃ -C ₆ H ₄	CH ₂ CO ₂ <i>t</i> Bu	98	98
13	4-CH ₃ -C ₆ H ₄	Ar'COCH ₂	97	99
14	4-CH ₃ -C ₆ H ₄	Ph COCH ₂	99	99

Ar'=3,4-(MeO)₂C₆H₃COCH₂

dried (MgSO₄) and the solvent evaporated. The product was >95% pure as found by TLC and ¹H NMR analyses. The product could be further purified by short path distillation or column chromatography.

Acknowledgement

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