



A highly efficient, green, rapid, and chemoselective oxidation of sulfides using hydrogen peroxide and boric acid as the catalyst under solvent-free conditions

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ABSTRACT

We report boric acid as a highly efficient and eco-friendly catalyst for the selective oxidation of sulfides to sulfoxides or sulfones, in excellent yields under solvent-free conditions, using 30% hydrogen peroxide as an oxidant. Various sulfides possessing functional groups such as alcohol, ester, and aldehyde are successfully and selectively oxidized without affecting sensitive functionalities.

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The chemoselective preparation of chiral and achiral sulfoxides and sulfones is extremely important in organic chemistry. Sulfoxides and sulfones are valuable intermediates for the synthesis of fine chemicals and biologically active compounds.¹ Furthermore, sulfoxidation catalysis has assumed relevance in the desulfurization of fuels, due to environmental constraints.²

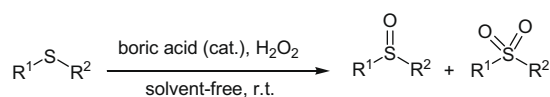
The main synthetic route for the preparation of these valuable materials is via oxidation of the corresponding sulfides. There are several reagents available for this key transformation which is typically achieved using stoichiometric or catalytic amounts of both organic and inorganic reagents.^{3–5}

The use of 'green oxidants' such as molecular oxygen and hydrogen peroxide is attractive, since they are readily available, inexpensive, and environmentally benign, with formation of water as the only by-product.⁶ Oxidation of sulfides with H₂O₂ is slow; hence extensive studies have been undertaken to develop new catalysts for this reaction.^{7–14,3} Disadvantages of this sulfoxidation reaction include difficulties in stopping the oxidation at the sulfoxide stage, utilization of environmentally unfavorable reagents, solvents, and catalysts, the preparation of complex catalysts, removal or recovery of the expensive catalyst, metal residues in the products, and the formation of large amounts of toxic waste. Hence

there is a need to develop new catalysts which can overcome these drawbacks.

Boric acid is commercially available, environmentally compatible, cheap, easy to handle, and stable. It was recently shown to be a good substitute for conventional acidic catalytic materials.^{15–19} The boric acid/H₂O₂ system offers an ideal combination for the chosen oxidations. For these reasons, and in continuation of our studies on environmentally benign chemical processes,^{20–22} we report the chemoselective oxidation of sulfides to sulfoxides or sulfones with H₂O₂ in the presence of a catalytic amount of boric acid by controlling the amount of H₂O₂ and catalyst (Scheme 1). First, in order to optimize the reaction conditions, we evaluated the influence of different amounts of hydrogen peroxide and catalyst on the oxidation of diphenyl sulfide, a relatively unreactive substrate, as a model compound in terms of time and product yield (Table 1).

As shown in Table 1, the reaction was incomplete in the absence of a catalyst even after 24 h (entries 3 and 8). When boric acid was



R¹, R² = Ar, benzylic, linear, cyclic

Scheme 1.

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Table 1

Optimization of the amounts of H₂O₂ and boric acid for the selective oxidation of diphenyl sulfide to diphenyl sulfoxide or diphenyl sulfone

Entry	H ₂ O ₂ (equiv)	Boric acid (mmol)	Time	Yield (%) ^a	
				Sulfoxide	Sulfone
1	0.6	0.1	30 min	50	—
2	1.2	0.1	5 min	100	—
3	1.2	0	24 h	80	—
4	1.2	0.02	30 min	40	—
5	1.2	0.05	30 min	70	—
6	2.4	0.2	60 min	—	70
7	3.6	0.2	25 min	—	100
8	3.6	0	24 h	—	50
9	3.6	0.05	60 min	—	30
10	3.6	0.1	60 min	—	65

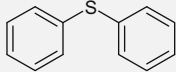
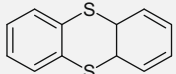
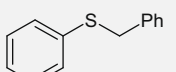
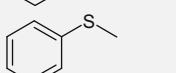
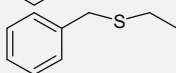
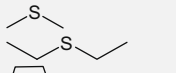
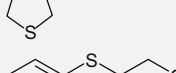
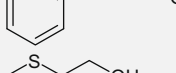
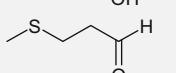
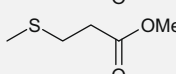
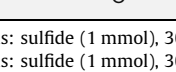
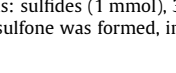
^a Conversions determined by GC.

added, the times were reduced considerably and the yield increased to 100%. H₂O₂ (1.2 equiv) in the presence of boric acid (0.1 mmol) was found to be ideal for the complete conversion of sulfides to sulfoxides. The use of excess H₂O₂ (3.6 equiv) in the presence of boric acid (0.2 mmol) led to the corresponding sulfone in a clean reaction.

In order to generalize the scope of the reaction, a series of structurally diverse sulfides was subjected to oxidation under the optimized reaction conditions, and the results are presented in Table 2.

Table 2

Selective oxidation of sulfides to sulfoxides or sulfones under solvent-free condition

Entry	Substrate	Sulfoxide ^a		Sulfone	
		Time (min)	Isolated yield (%)	Time (min)	Isolated yield (%)
1		Immediate	95	25	95 ^b
2		15	92 ^d	90	94 ^{b,d}
3		Immediate	93	30	90 ^b
4		Immediate	94	30	94 ^b
5		Immediate	91	20	92 ^b
6		12	87	150	89 ^c
7		15	90	135	92 ^c
8		10	89	180	87 ^c
9		20	89	90	90 ^c
10		Immediate	86	210	87 ^c
11		Immediate	88	180	No reaction
12		Immediate	85	180	No reaction

^a Reaction conditions: sulfide (1 mmol), 30% H₂O₂ (1.2 equiv), boric acid (10 mol %), rt.

^b Reaction conditions: sulfide (1 mmol), 30% H₂O₂ (3.6 equiv), boric acid (20 mol %), rt.

^c Reaction conditions: sulfides (1 mmol), 30% H₂O₂ (4.8 equiv), boric acid (30 mol %), rt.

^d The disulfoxide/disulfone was formed, in the case of disulfoxide on the basis of melting point, compared with an authentic sample, its stereochemistry was *trans*.²³

The expected products were obtained in short times and in high yields. It is notable that the sulfides were oxidized chemoselectively in the presence of oxidation-prone functional groups such as OH, and CHO (Table 2, entries 9–11). An ester group also remained intact during the reaction (Table 2, entry 12).

In order to establish the catalytic activity of boric acid, we compared our results on the oxidation of diphenyl sulfide with data from the literature (Table 3). As shown in Table 3, the previously reported procedures suffer from one or more disadvantages such as elevated reaction temperatures,^{11,13,14} longer reaction times,^{11,14} special efforts for the preparation of catalyst,^{11–13} using a transition metal,^{10,14} and the need for volatile and toxic organic solvents.^{10–14}

This procedure offers several major advantages: (1) the use of a commercially available, cheap, and chemically stable catalyst and oxidant; (2) highly efficient for the selective oxidation of structurally diverse sulfides in good to high yields; (3) control over the degree of oxidation offers access to sulfoxides or sulfones; (4) excellent chemoselectivity; and (5) the method conforms to several of the guiding principles of green chemistry. We believe the present method to be an improvement with respect to other procedures.

General procedure for the oxidation of sulfides to sulfoxides. The sulfide (1 mmol) was added to a solution of 30% H₂O₂ (1.2 equiv, 0.5 g) and boric acid (0.1 mmol, 0.006 g), and the mixture was stirred at room temperature for the time specified in Table 2. The

Table 3Comparison of the activity of various catalysts in the oxidation of diphenyl sulfide using H₂O₂

Entry	Catalyst	Sulfoxide			Sulfone			Ref.
		Conditions	Time (h)	Yield (%)	Conditions	Time (h)	Yield (%)	
1	H ₃ BO ₃	Neat, rt	Immediate	95	Neat, rt	0.6	95	This work
2	MoO ₂ Cl ₂	Acetone, rt	0.35	89	CH ₃ CN, rt	0.55	91	10
3	H ₅ PMo ₁₁ Al _{0.5} V _{0.5} O ₄₀	CH ₃ CN, reflux	2	100	CH ₃ CN, reflux	4	95	11
4	Silica sulfuric acid	CH ₃ CN, rt	6	95	CH ₃ CN, rt	0.75	95	12
5	Carbon-based solid acid	C ₂ H ₄ Cl ₂ , reflux	0.17	98	C ₂ H ₄ Cl ₂ , reflux	0.17	95	13
6	TaCl ₅	CH ₃ CN or <i>i</i> -PrOH or <i>t</i> -BuOH, rt	2	90	CH ₃ OH, reflux	3.5	90	14

progress was monitored by TLC or GC. After completion of the reaction, the product was extracted with CH₂Cl₂ (3 × 10 mL) and the combined organics was washed with brine (15 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to give the corresponding pure sulfoxide in most cases. Further purification was achieved by short-column chromatography on silica gel with EtOAc/*n*-hexane (1/10) as eluent. All the products are known and were characterized by IR, ¹H NMR, and by melting point comparisons with those of authentic samples.^{8,23–26}

General procedure for the oxidation of sulfides to sulfones. The sulfide (1 mmol) was added to a solution of 30% H₂O₂ (3.6–4.8 equiv) and boric acid (0.2–0.3 mmol), and the mixture was stirred at room temperature for the time specified in Table 2. The progress was monitored by TLC or GC. After completion of the reaction, the product was extracted with CH₂Cl₂ (3 × 10 mL) and the combined organics was washed with brine (15 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to give the corresponding pure sulfone in most cases. Further purification was achieved by recrystallization from EtOH. All the products are known and were characterized by IR, ¹H NMR, and by melting point comparisons with those of authentic samples.^{7,8,25}

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