

Rapid and highly chemoselective biomimetic oxidation of organosulfur compounds with tetrabutylammonium peroxymonosulfate in the presence of manganese *meso*-tetraphenylporphyrin and imidazole

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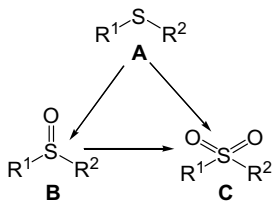
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Received 15 January 2004; revised 1 March 2004; accepted 12 March 2004

Abstract—A novel and efficient method is described for the immediate oxidation of different organosulfur compounds using tetrabutylammonium peroxymonosulfate in the presence of manganese *meso*-tetraphenylporphyrin and imidazole. The method is highly chemoselective and the yields are excellent.

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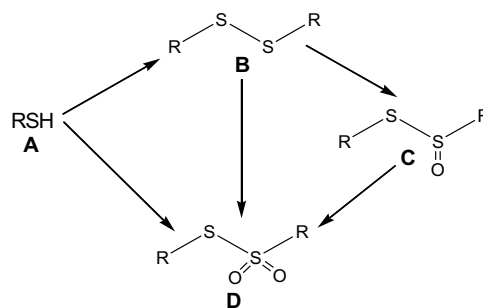
The oxidation of organosulfur compounds, which are a major source of environmental pollution, is very important from both industrial and green chemistry points of view.¹ On the other hand, their oxidation products are useful precursors for biologically and chemically important compounds.^{2,3} For example, sulfones (C, Scheme 1) and thiosulfonates (D, Scheme 2), both of which occur in some pharmaceuticals,⁴ have been extensively used as versatile intermediates in organic synthesis.^{5,6} Recently, sulfones have been employed for stabilizing α -radicals,⁷ α -anions,⁸ and acting as cationic synthons.⁹ Thiosulfonates, with strong sulfenylating power, have found wide industrial applications both in polymer production and in photographic processes.¹⁰



Scheme 1.

Keywords: Sulfone; Thiosulfonate; Tetrabutylammonium peroxymonosulfate; Manganese porphyrin.

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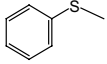
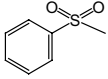
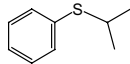
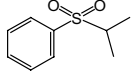
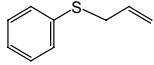
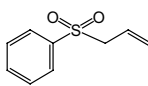
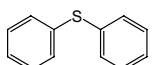
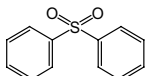
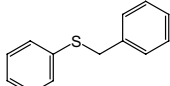
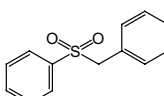
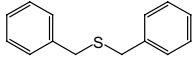
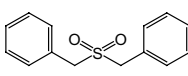
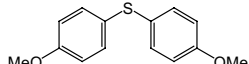
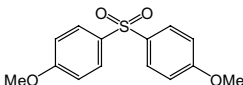
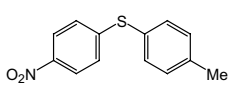
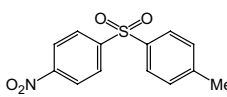
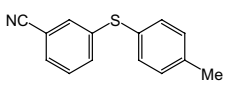
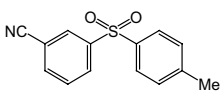
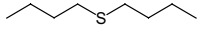
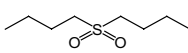
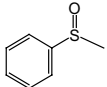
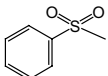
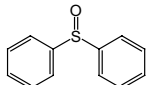
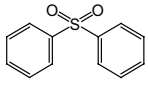
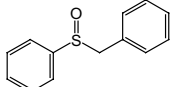
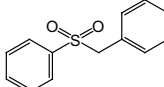


Scheme 2.

Decontamination procedures require very fast and selective chemical transformations. In this regard, many efficient catalysts for oxidative degradation of various types of pollutants and residual wastes have been developed.^{4b,11} Biomimetic catalysts, in particular metalloporphyrins, have been of considerable interest for chemoselective oxidation of organosulfur compounds,¹² especially with respect to the catalytic role of cytochrome P-450 and vitamin B₁₂ in the oxidation of biological sulfides and thiols.¹³

In the course of our studies on tetrabutylammonium peroxymonosulfate (TBAO) for oxidation of organic compounds, we have explored it as an efficient oxidant for the selective transformation of imines to oxaziridines.¹⁴ Its use in oxyfunctionalization of hydrocarbons required activation by Mn-porphyrin.¹⁵ TBAO has also

Table 1. TBAO oxidation of sulfides,^a and sulfoxides,^b to sulfones catalyzed by Mn(TPP)OAc in the presence of Im

Entry	Substrate	Conversion%	Product	Yield% ^c (Isolated) ^d	Time (min)
1		100		100 (96)	<1
2		100		100	<1
3		100		100	<1
4		100		100	<1
5		100		100 (95)	<1
6		100		100 (93)	<1
7		100		100 (96)	<1
8		100		100 (92)	3
9		100		100 (95)	3
10		100		100	<1
11		100		100	<1
12		100		100	<1
13		100		100	<1

^a The molar ratio for sulfide/TBAO/Im/Mn(TPP)OAc is 100:100:20:1.

^b The molar ratio for sulfoxide/TBAO/Im/Mn(TPP)OAc is 100:50:20:1.

^c The yields were based on the starting substrates determined by GLC (entries 1–4, 10–12) or ¹H NMR (entries 5–9, 13). The identity of products were confirmed by comparison of their spectral data with known samples prepared according to the literature.^{18,11g}

^d Isolated by silica gel column chromatography.

been introduced as a very sluggish oxygen source for the oxidation of sulfides to sulfones (**A** → **C**, Scheme 1).¹⁶ For example, oxidation of thioanisole by 3 equiv of TBAO took four days to produce a 78% yield of the

corresponding sulfone. We found that the addition of only 1 mol% of commercially available manganese *meso*-tetraphenylporphyrin in the presence of imidazole (Im) as co-catalyst, considerably improved the rate of

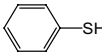
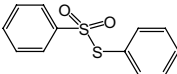
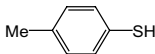
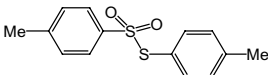

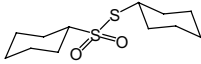
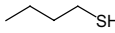
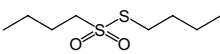

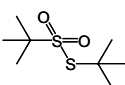
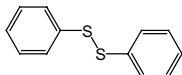
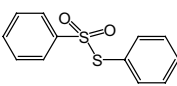
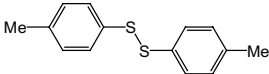
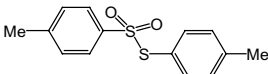
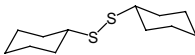
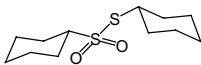
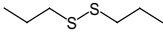
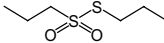
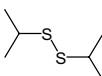
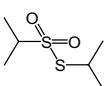
conversion (<3 min) and selectivity of sulfone formation (100%) using α -stoichiometric amount of freshly prepared TBAO,^{16,17} at room temperature (**A** \rightarrow **C**, Scheme 1).

This catalytic system is very efficient for the oxygenation of sulfides to sulfones (Table 1).¹⁹ It leads to the complete conversion of dialkyl, phenyl alkyl, phenyl allyl, diphenyl, benzyl phenyl and dibenzyl sulfides to the corresponding sulfones in excellent yields (100%) and excellent selectivities (100%) within 1 min at room temperature. Despite the efficiency of this method for the epoxidation of alkenes,¹⁵ a sulfide also having a carbon–carbon double bond (entry 3), was cleanly transformed into the corresponding sulfone in excellent yield.^{11c} In addition, benzyl phenyl and dibenzyl sulfides (entries 5 and 6) were selectively oxidized to their corresponding

sulfones without formation of any benzylic oxidation by-products.

The notable feature of this method is the efficient oxidation of electron-deficient sulfides to sulfones. Most of the reported methods for this purpose,²⁰ have some limitations such as low yields or use of reagents, which require special handling.^{11h} Sulfides having electron-withdrawing substituents such as 4-nitrophenyl 4-methylphenyl sulfide and 3-cyanophenyl 4-methylphenyl sulfide (entries 8 and 9), reacted completely within 3 min with 100% selectivity for formation of their corresponding sulfones. Oxidation of the electron-rich sulfide, di-4-methoxyphenyl sulfide (entry 7) gave the related sulfone as the sole product. This catalytic system is also applicable to the efficient and rapid oxidation of sulfoxides to sulfones (**B** \rightarrow **C**, Scheme 1, entries 11–13).

Table 2. TBAO oxidation of thiols^a and disulfides^b to thiosulfonates catalyzed by Mn(TPP)OAc in the presence of Im

Entry	Substrate	Conversion%	Product	Isolated yield% ^c	Time (min)
1		100		96	<1
2		100		94 (100) ^d	<1
3		100		93	<1
4		100		94	<1
5		100		95 (100) ^d	3 ^e
6		100		97	<1
7		100		95 (100) ^d	<1
8		100		96	<1
9		100		94	<1
10		100		92 (100) ^d	<1

^a The molar ratio for thiol/TBAO/Im/Mn(TPP)OAc is 100:150:40:1.

^b The molar ratio for disulfide/TBAO/Im/Mn(TPP)OAc is 100:100:20:1.

^c The products were isolated by column chromatography and identified by comparison with known samples.²¹

^d ¹H NMR yields based on the starting materials.

^e Conversion (100%) was observed within 1 min with the formation of 75% of thiosulfonate; δ_{H} (ppm): 1.42, 1.60 along with 25% of thiosulfinate; δ_{H} (ppm): 1.38, 1.56,²² using ¹H NMR (250 MHz) analysis.

Structurally different sulfoxides were readily oxidized to their corresponding sulfones under the same reaction conditions as sulfides, using 0.5 equiv of TBAO.

From the standpoint of methodology, the one pot transformation of thiols to thiosulfonates (**A** → **D**, Scheme 2) has been of interest.²³ Using this catalytic system, a variety of aromatic and aliphatic thiols were rapidly oxidized to their corresponding thiosulfonates with excellent yields and selectivities at room temperature (Table 2, entries 1–5).²⁴

It is notable that oxidation of the sterically more demanding *t*-butylmercaptan (entry 5) also gave only the related thiosulfonate product,^{11c} however, it required a 3 min reaction time.

With regards to the fast and quantitative oxidation of thiols, it is expected that disulfides should also be easily oxidized to their corresponding thiosulfonates (**B** → **D**, Scheme 2) by this simple method.²⁵ Inspection of our results in Table 2 (entries 6–10) shows high chemoselectivity for the conversion of some symmetric aryl and alkyl disulfides to the corresponding thiosulfonates without the formation of any thiosulfinate (**C**, Scheme 2) product.

This oxidation system can also be used for oxidative coupling of thiols to symmetrical disulfides (**A** → **B**, Scheme 2) under controlled conditions using a smaller amount of Im. The gradual addition of a solution of TBAO (0.25 mmol in 2 mL CH₂Cl₂) over a 30 min period to a cooled solution (–5 °C) of 4-methylbenzenethiol (Table 2, entry 2, 0.1 mmol), Im (0.01 mmol) and Mn(TPP)OAc (0.001 mmol) in 2 mL CH₂Cl₂ gave a 90% yield of the corresponding symmetrical disulfide along with a small percentage of the related thiosulfonate (10%) determined by ¹H NMR analysis. It was also observed that the molar ratio of catalyst versus substrate has a significant effect upon the selectivity of the oxidation reactions. For example, the use of 0.0, 0.01, 0.02, 0.1 and 1 mol% of Mn(TPP)OAc in the oxidation of thioanisole (Table 1, entry 1) led to sulfoxide/sulfone molar ratios of 0.8, 0.15, 0.12, 0.09 and 0.0, respectively. It seems to us that the isolation of the intermediate products [sulfoxide (**B**, Scheme 1) and thiosulfinate (**C**, Scheme 2)] could be possible under controlled conditions. Further investigations in this regard are underway.

In conclusion, the remarkable efficiency of Mn^{III} meso-tetraphenylporphyrin in the presence of Im for the extremely rapid and highly chemoselective oxidation of different organosulfur groups with TBAO under very mild reaction conditions is described.

Acknowledgements

The research was supported by the Shiraz University Research Council.

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 24. *General procedure*: TBAO (1.5 mmol) was added to a solution of thiol (1 mmol), Im (0.4 mmol), Mn(TPP)OAc (0.01 mmol) in CH₂Cl₂ (5 mL) and the mixture stirred under air at room temperature. The reaction was followed by TLC and the yield of product was determined by ¹H NMR analysis of the reaction mixture or after purification by chromatography over silica gel (eluent: cyclohexane/ethyl acetate 90:10).
 25. The procedure is similar to that mentioned in Ref. 19 only for disulfides instead of sulfides.