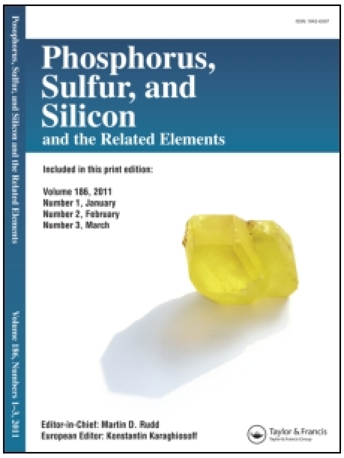

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1,2-Dipyridiniumditribromide-ethane (DPTBE) as a New Oxidizing Agent for the Chemoselective Oxidation of Sulfides to the Sulfoxides

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1,2-DIPYRIDINIUMDITRIBROMIDE-ETHANE (DPTBE) AS A NEW OXIDIZING AGENT FOR THE CHEMOSELECTIVE OXIDATION OF SULFIDES TO THE SULFOXIDES

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A wide range of aliphatic or aromatic sulfides is selectively oxidized to the corresponding sulfoxides using 1,2-dipyridiniumditribromide-ethane (DPTBE) in a mixture of CH_2Cl_2/H_2O under heterogeneous conditions in moderate to high yields.

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

Keywords 1,2-Dipyridiniumditribromide-ethane (DPTBE); oxidation; sulfides; sulfoxides

INTRODUCTION

The chemistry of sulfoxides has been attractive to organic chemists. Interest in the chemistry of sulfoxides is due to the fact that sulfoxides are important synthetic intermediates in the preparation of biologically and medicinally useful compounds.[1–3] Sulfoxides have also been used extensively in C—C bond-forming, molecular rearrangements, and functional group transformations.[4–8]

There are several reports on the oxidation of sulfides to the sulfoxides with molecular bromine.[9–12] However to decrease the toxicity of molecular bromine, a wide variety of organic tribromide reagents were reported and applied in different functional group transformations.[13–21] Also, recently we have synthesized ($\{[K.18\text{-crown-6}]Br_3\}n$); this reagent was applied for the oxidative coupling of thiols and bromination of some aromatic compounds.[22]

Although a number of methods for sulfoxidation have emerged in recent years,[23–34] the development of environmentally benign oxidants has become increasingly important.

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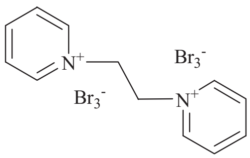


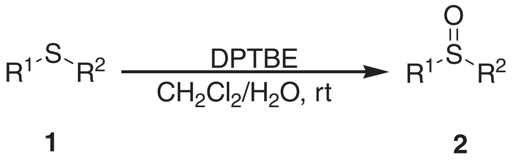
DPTBE

Figure 1 1,2-Dipyridiniumditribromide-ethane.

RESULTS AND DISCUSSION

In continuation of our studies on the application of new oxidizing reagents in organic transformations,[35–41] we became interested in introducing a new oxidizing media, based on in situ generation of Br_2 with 1,2-dipyridiniumditribromide-ethane (DPTBE) (Figure 1) as a new oxidizing agent.

1,2-Dipyridiniumditribromide-ethane has been synthesised previously by Kavala et al.[42] and has been applied for the bromination of a wide variety of organic compounds. In this communication, we decided to apply 1,2-dipyridiniumditribromide-ethane DPTBE for the oxidation of different types of sulfides **1** to the corresponding sulfoxides **2** in a mixture of dichloromethane and H_2O at room temperature with reasonable yields (Scheme 1 and Table I).



Scheme 1 Oxidation of sulfides into sulfoxides.

Sulfoxidation reactions were selectively carried out under mild conditions, and no impurity of sulfone was observed whatsoever. The catalytic oxidation procedure is very simple, and the products are easily isolated from the reaction media by simple filtration and evaporation of dichloromethane.

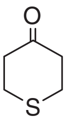
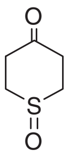
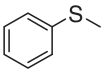
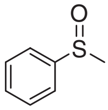
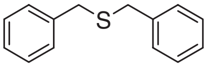
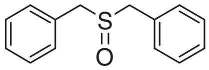
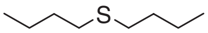
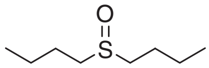
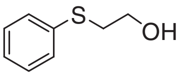
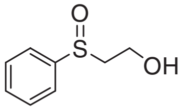
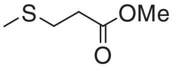
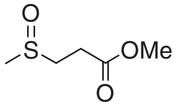
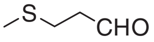
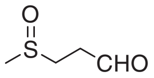
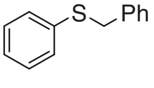
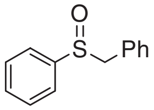
To investigate the chemoselectivity of the described system, a sulfide containing an alcohol group was subjected to the sulfoxidation reaction, but alcohol oxidation did not occur under the above-mentioned conditions, and the primary hydroxyl groups remained intact during the reaction (Table I, entry 5, and Scheme S1, available online in the Supplemental Materials).

A plausible mechanism of this oxidation is shown in Scheme S2 (see the Supplemental Materials online) based on the reported pathway in the literature,[37,43] our observations, and obtained results.

To show the efficiency of the described system in comparison with previously reported bromine-containing reagents, we compared our obtained results for the oxidation of dibutyl sulfide and dibenzyl sulfide with the best of the well-known data from the literature, as shown in Table II.

Initially, a reaction between an organic sulfide and bromine (from DPTBE) produces bromosulfonium as an unstable intermediate. Finally in the presence of water, bromosulfonium decomposes to the corresponding sulfoxide.

Table I Oxidation of sulfides **1** to the corresponding sulfoxides **2** using 1,2-dipyridiniumditribromide-ethane DPTBE in CH_2Cl_2/H_2O at room temperature[a]

Entry	Substrate	Substrate	Time (min)	Yield (%)[b]	Ref. [c]
1			20	73	44
2			5	87	45–46
3			10	90	27, 44–46, 48
4			10	93	27, 44–46, 48
5			20	79	46, 48
6			15	85	46
7			5	45	46, 47
8			12 h	78	27, 44–48

[a] Substrate/DPTBE for entries 1–7 = 1 mmol: 0.7 g; for entry 8 = 1 mmol: 0.9 g.

[b] Isolated yield after short column chromatography.

[c] All products are known and were identified using comparison of their physical and spectral data (IR, NMR, or MS) with those reported in the literature.

Table II Comparison of the different methods used for the oxidation of dibutyl sulfide and dibenzyl sulfide

Entry	Substrate	Reagent	Time (min)	Yield (%)[a]	Ref.
1	Dibutyl sulfide	DPTBE	10	93	This work
2	Dibenzyl sulfide	DPTBE	10	90	This work
3	Dibutyl sulfide	1,4-iazabicyclo(2,2,2) octane tribromide	—	85	9
4	Dibutyl sulfide	Pyridinium tribromide	80	99	13
5	Dibenzyl sulfide	Cetyltrimethylammonium tribromide	120	92	14
6	Dibutyl sulfide	1-Benzyl-4-aza-1-azonia-bicyclo[2.2.2] octane tribromide	2	95	49

[a] Isolated yield.

In summary, we report in this article an efficient method for the selective oxidation of sulfides to sulfoxides under very mild conditions with moderate to good yields. This method offers the advantage of shorter reaction times, high selectivity, cost effective reagents, and easy workup.

EXPERIMENTAL

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. The oxidation products were characterized by comparison of their spectral (IR, ^{1}H NMR, and ^{13}C NMR) and physical data with authentic samples. 1,2-Dipyridiniumditribromide-ethane (DPTBE) was prepared via a reported procedure by Kavala et al.[42]

Oxidation of Dibenzyl Sulfide to Dibenzyl Sulfoxide: Typical Procedure

DPTBE (0.7 g) was added to a solution of dibenzyl sulfide (0.214 g, 1 mmol) in CH_2Cl_2 (8 mL) and H_2O (8 mL). This reaction mixture was stirred at room temperature for 10 min (the reaction progress was monitored by TLC) and then filtered. The residue was washed with CH_2Cl_2 (20 mL). Anhydrous Na_2SO_4 (4 g) was added to the filtrate and filtered off after 20 min, then CH_2Cl_2 was removed by a water bath (40–50°C) and simple distillation. The crude product was purified by flash silica gel column chromatography using acetone:*n*-hexane (4:6) as an eluent, and the pure product was obtained in 90% yield (0.207 g).

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