

## Selective and mild oxidation of sulfides to sulfoxides by H<sub>2</sub>O<sub>2</sub> using DBUH-Br<sub>3</sub> as catalyst

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### Abstract

DBUH-Br<sub>3</sub> catalyzed selective conversion of sulfides to sulfoxides in the presence of H<sub>2</sub>O<sub>2</sub> as oxidizing agent is described. The reaction was performed selectively at room temperature and relatively short reaction times.

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*Keywords:* Sulfide; Sulfoxide; Selective oxidation; H<sub>2</sub>O<sub>2</sub>; DBUH-Br<sub>3</sub>

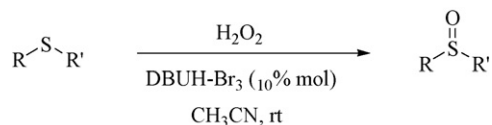
Sulfoxides are important intermediates in the synthesis of various natural products [1,2]. Omeprazole and Figpronil pesticides are two typical examples of extensive applications of these important intermediates in pharmaceutical and fine chemical industries [3]. Syntheses of sulfoxides are usually achieved by oxidation of their corresponding sulfides. During the last years, various procedures for H<sub>2</sub>O<sub>2</sub> oxidation of sulfides including the use of various heterogeneous catalyst systems have been reported [4–6]. The application of this oxidant has been developed due to its effective oxygen content, eco-friendly nature, low cost, and also safety in storage and operation [7,8]. Recently various heterogeneous catalyst-oxidizing agent systems including gold(III)–hydrogen peroxide [9], silica-immobilized vanadyl alkyl phosphonate–sodium bromate [10], silica sulfuric acid–hydrogen peroxide [11], and titanium based catalyst-oxidizing agents have been reported for oxidation of sulfides. Although, many reagents have been employed for the oxidation of sulfides to sulfoxides, the most common problem encountered during the reaction is the over-oxidation of sulfoxides to their corresponding sulfones [12]. Prompted by these reports and due to the potential oxidation of sulfur-containing compounds by H<sub>2</sub>O<sub>2</sub> in the presence of heterogeneous catalysts, in this study we wish to report on a new and efficient method for selective oxidation of sulfides to sulfoxides by H<sub>2</sub>O<sub>2</sub> as oxidant and in the presence of DBUH-Br<sub>3</sub> as catalyst (Scheme 1).

### 1. Experimental

All chemicals were purchased from Merck and Fluka chemical companies. The oxidation products were characterized by comparison of their spectral and physical data with authentic samples.

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Scheme 1.

### 1.1. General procedure for the selective oxidation of sulfides to sulfoxides

To a mixture of various sulfides (1 mmol) and DBUH-Br<sub>3</sub> (0.1 mmol, 0.039 g) in CH<sub>3</sub>CN (15 mL), H<sub>2</sub>O<sub>2</sub> 30% (v/v) (1.4 mmol) was added gradually. After the completion of the reaction which was monitored by TLC using n-hexane: EtOAc (7:3), the solvent was removed and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added and the mixture was washed with water (15 mL), 5% HCl solution (15 mL) and water (15 mL), respectively. The organic phase was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The resulting products were determined by their <sup>1</sup>H NMR spectrums and compared with the authentic samples.

## 2. Results and discussion

The synthesis and X-ray structure of DBUH-Br<sub>3</sub> as the catalyst have already been reported elsewhere (Fig. 1) [13].

In order to get an insight into the optimum catalytic conditions for the selective oxidation of sulfides to sulfoxides, the oxidation reaction of methylphenylsulfide by hydrogen peroxide as a model experiment was studied at different temperatures and catalyst/H<sub>2</sub>O<sub>2</sub> ratios. The results are summarized in Table 1. Different solvents were also screened

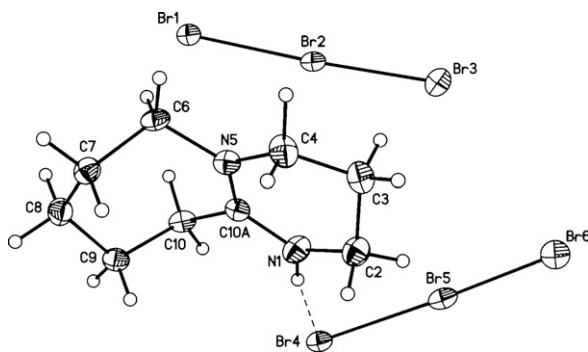


Fig. 1. Molecular structure and atomic labeling scheme (50% probability level).



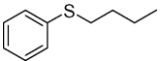
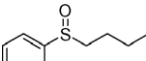
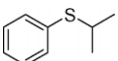
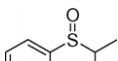
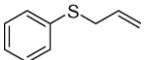
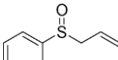
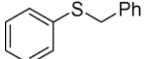
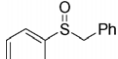
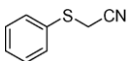
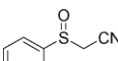
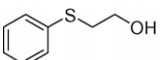
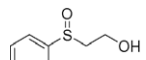
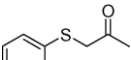
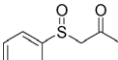
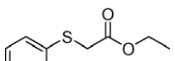
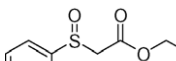
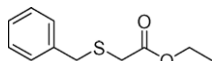
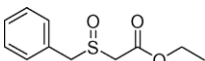
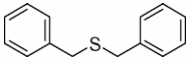
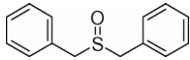
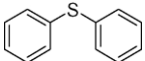
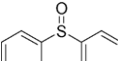
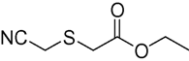
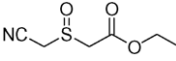
Table 1

The data for optimization of oxidation of methylphenylsulfide using H<sub>2</sub>O<sub>2</sub>.<sup>a</sup>

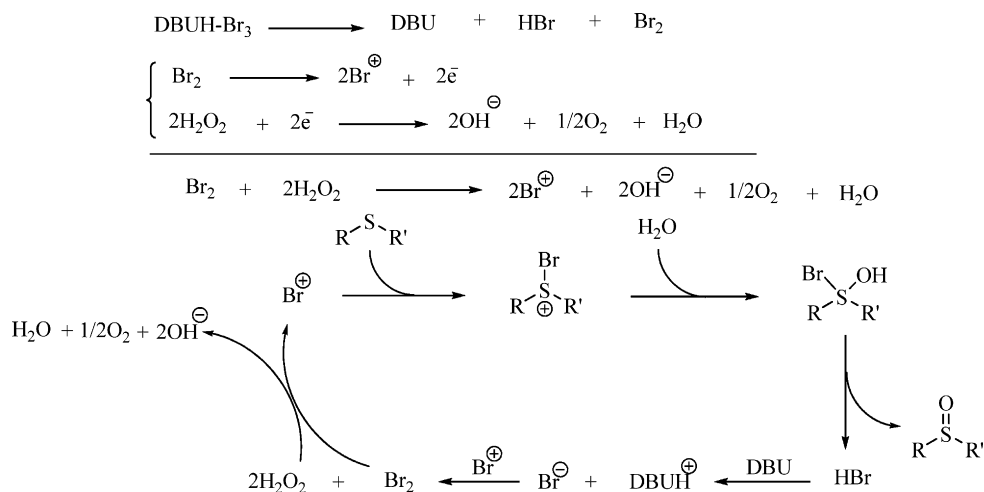
Entry	Catalyst (mol%)	H <sub>2</sub> O <sub>2</sub> (mmol)	Temperature (°C)	Sulfide (%)	Sulfoxide (%)	Sulfone (%)
1	50	1.4	25	0	82	18
2	30	1.4	25	0	100	0
3	15	1.4	25	0	100	0
4	10	1.4	25	0	100	0
5	5	1.4	25	79	21	0
6	0	1.4	25	75	25	0
7	10	0	25	88	12	0
8	10	1.9	25	14	81	5
9	10	1.4	25	0	100	0
10	10	0.8	25	84	16	0
11	10	1.4	40	0	100	0
12	10	1.4	60	0	100	0
13	10	1.4	Reflux	0	89	11

<sup>a</sup> Selectivities are based on <sup>1</sup>H NMR spectroscopic integration.

Table 2  
 Selective oxidation of various functionalized substrates to sulfoxides using H<sub>2</sub>O<sub>2</sub> in the presence of DBUH-Br<sub>3</sub>.

Entry	Substrate	Product	Time (min)	Yield (%) <sup>a</sup>	[lit.]
1			60	95	[14]
2			60	90	[15]
3			120	80	[16]
4			150	85	[17]
5			45	90	[17]
6			100	95	[18]
7			150	66	[19]
8			90	75	[20]
9			120	80	[17]
10			100	75	[17]
11			90	95	[21]
12			100	85	[19]
13			150	70	[18]

<sup>a</sup> Isolated yield.



Scheme 2.

for the oxidation of methylphenylsulfide, and as the result acetonitrile was found to be the best solvent in terms of activity and selectivity.

In order to show the catalytic role of DBUH-Br<sub>3</sub>, the reaction of methylphenylsulfide was performed in the absence of DBUH-Br<sub>3</sub>. The reaction was not completed within 24 h (Table 1, entry 6). Consequently, it was performed in different molar ratios of the catalyst in the presence of oxidant in order to obtain the optimum reaction conditions (Table 1, entries 1–5).

The chemoselectivity of the system was also investigated. Several sulfides containing an unsaturated C–C bond, nitrile or an alcoholic group were subjected to the sulfoxidation reaction, and it was observed that the functional groups remained intact during the reaction (Table 2, entries 4, 6, 7, 13).

The suggested mechanism of this selective oxidation is shown in Scheme 2. DBUH-Br<sub>3</sub> might *in situ* generate Br<sub>2</sub>. Subsequently, Br<sup>+</sup> can be produced *via* oxidation with H<sub>2</sub>O<sub>2</sub>. The final step of oxidation involves nucleophilic attack of sulfur of the sulfide compound on the Br<sup>+</sup> followed by concerted oxygen transfer from water to give the corresponding sulfoxide.

In summary, we have described an efficient method for the selective oxidation of sulfides to sulfoxides under very mild reaction conditions. Also, chemoselectivity, easy and clean work-up, green oxidant, high yields and the easy preparation of the catalyst were the remarks of this method which could be the priority of the other existing methodologies.

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