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# PyHBr<sub>3</sub>/TBN/H<sub>2</sub>O as catalytic system for the oxidation of sulfides to sulfoxides with air as the oxidant

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#### ARTICLE INFO

## ABSTRACT

for the oxidation discussed in this Letter.

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Introduction

The oxidation of sulfides to their corresponding sulfoxides is one of the most important transformations in the synthesis of different organisms. Sulfoxides can be used as synthetic intermediates for the construction of various chemically and biologically significant molecules,<sup>1,2</sup> as well as oxidant for the oxidation of alcohols.<sup>3</sup> Therefore, different methods have been developed to oxidize various sulfides. However, most of the methods need a stoichiometric amount of oxidants.<sup>4,5</sup> In recent years, hydrogen peroxide and molecular oxygen as oxidant have attracted much attention<sup>6-10</sup> and have been extensively developed due to environmental protection, low cost, easy handling, safe storage, and producing water as the only by-product. Unfortunately, hydrogen peroxide being a kind of strong oxidizing agent, sometimes is hard to control, and over-oxidation occurs easily in the reactions.<sup>11-14</sup> Compared with hydrogen peroxide, molecular oxygen is easily controlled. In the previous reports, a lot of high-efficiency catalyst systems, such as the rhenium,<sup>15</sup> ruthenium,<sup>16</sup> palladium,<sup>17</sup> cobalt,<sup>6</sup> copper,<sup>18,19</sup> iron,<sup>20</sup> and gold<sup>21</sup> were used in the reactions with molecular oxygen as oxidant. However, transition metal catalysts are commonly expensive and it may also be hard to be removed from the reaction substrates, which might lower the purity of the products. Therefore, the new catalysts with no transition metal, will be of great value.



Pyridinium bromide perbromide (PyHBr<sub>3</sub>) and *tert*-butyl nitrite (TBN) catalytic system was used for the

oxidation of sulfides with air as the oxidant. Under mild conditions (at room temperature), a series of sul-

fide substrates have been oxidized to their corresponding sulfoxides with high conversion rate. To the

best of our knowledge, for the first time, the PyHBr<sub>3</sub>/TBN/H<sub>2</sub>O is reported as exceptional catalyst system

Scheme 1.

Our research was initially inspired by the mechanism of selective catalysis of sulfide oxidations from Ref. 22, in which Bosch et al. reported that, by using dioxygen and catalytic amounts of nitrogen dioxide, the alkyl and aryl thioethers can be oxidized into their corresponding sulfoxides. Our group has carried out some relative research work<sup>23–25</sup> and found DBDMH/NaNO<sub>2</sub>, Br<sub>2</sub>/NaNO<sub>2</sub>/ H<sub>2</sub>O, and HBr/*t*-BuONO catalyst systems for catalysis of the aerobic oxidation of a wide range of sulfides. Meanwhile, it has been reported the use of pyridinium bromide perbromide as oxidant for the oxidation of sulfides and alcohols.<sup>26,27</sup> In this Letter, a novel metal-free catalytic system PyHBr<sub>3</sub>/TBN/H<sub>2</sub>O was applied for the oxidation of sulfides to their corresponding sulfoxides with air as the terminal oxidant at room temperature (Scheme 1). This catalytic system is reported for the first time.

## **Results and discussion**

The initial experiment was carried out using methyl phenyl sulfide as the substrate with different catalytic systems: PyHBr<sub>3</sub>/H<sub>2</sub>O, *tert*-butyl nitrite(TBN)/H<sub>2</sub>O, PyHBr<sub>3</sub>/TBN, and PyHBr<sub>3</sub>/TBN/H<sub>2</sub>O,





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Table 1 The catalysts' effect on the reaction<sup>a</sup>

Entry	PyHBr <sub>3</sub> (mol %)	t-BuONO (mol %)	$H_2O(ml)$	Conversion <sup>b</sup> (%)
1	3	0	1	0
2	0	4	1	0
3	3	4	0	73
4	3	4	1	100

<sup>a</sup> Reaction conditions: methyl phenyl sulfide (10 mmol), PyHBr<sub>3</sub> (0.3 mmol, 0.096 g), *t*-BuONO (0.4 mmol, 50 μl), H<sub>2</sub>O (1 ml), CH<sub>3</sub>CN (20 ml), air, 25 °C. Conversions were determined by GC with area normalization.

Table 2	2
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respectively at 25 °C for 3 h in CH<sub>3</sub>CN solution. TBN as a source of NO has easy accessibility and has unique oxidation ability. The results are listed in Table 1. The entries 1 and 2 showed the first two catalytic systems have no catalysis activities. Entry 3 showed better conversion, which indicated the PyHBr3 requiring a co-catalyst to activate the molecular oxygen and reoxidize the HBr to Br<sub>2</sub>, and then  $Br_2$  can oxidize the sulfide to the corresponding sulfoxide. The 3 mol % of PyHBr<sub>3</sub>, 4 mol % of TBN, and 1 ml of  $\ddot{H_2O}$  system show the most effective catalytic activity (entry 4), which were applied to all the experiments below.

Entry	Substrate	Product	Time (h)	Conversion <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1	S_	O S	3	>99	91
2	S S	L S	3	>99	92
3			5	>99	94
4	F	F S	3	>99	84
5	CI S	CT S	4.5	>99	91
6	of the second se		7.5	>99	71
7	O <sub>2</sub> N	O2N S	11	>99	88
8	S_ O		5	>99	93
9	C CI		9.5	>99	90
10	C S S		24	10	8
11	SS		2	>99	92
12	ССССАН	ОН	4	95	80

а Reaction conditions: substrates (10 mmol), PyHBr3 (0.3 mmol, 0.096 g), t-BuONO (0.4 mmol, 50 µl), H2O (1 ml), CH3CN (20 ml), air, 25 °C.

<sup>b</sup> Conversions were determined by GC with area normalization.



Scheme 2.

10 mmol substrates of methyl phenyl sulfide analogues were reacted with 3 mol % PyHBr<sub>3</sub>, 4 mol % of TBN, and 1 ml H<sub>2</sub>O in 20 ml CH<sub>3</sub>CN at 25 °C with air as oxidant, in which, good conversion rates were found, as shown in Table 2.

With this oxidation system, a variety of sulfides were successfully converted to sulfoxides with high conversion rate. From Table 2, it has been found that most of the substrates including electron-rich and nucleophilic-rich aromatic compounds take more time in the reaction than methyl phenyl sulfide. Substrates with electron-withdrawing groups take more time than those with electron-donating groups. This oxidation system did not show a good oxidation for diphenyl sulfide (entry 10). As we all know, 2-(phenylthio)ethanol (entry 12) has both the sulfide and hydroxyl functional groups, which may also be oxidized simultaneously. But this catalytic system has achieved the selective oxidation of the sulfide without oxidizing the hydroxyl group.

A possible mechanism for this new transition-metal-free catalytic oxidation process can be described by the dual cycle shown in Scheme 2. Firstly, sulfide was oxidized to the sulfoxide with Br<sub>2</sub> as the oxidant provided by the composition of PyHBr<sub>3</sub>, in this reaction H<sub>2</sub>O can provide the oxygen atom which is needed for the oxidation of sulfide to sulfoxide. Secondly, through cycle I, the Br<sup>-</sup> is continuously reoxidized to Br<sub>2</sub> by NO<sub>2</sub>, which is the key for a catalytic amount of Br<sub>2</sub> to oxidize sulfide substrates, meanwhile, the NO<sub>2</sub> is reduced to NO. The NO is easily released from TBN as an efficient NO equivalent and NO can easily be oxidized to NO<sub>2</sub> by O<sub>2</sub> through cycle II, at this cycle  $H^+$  are easy turn to H<sub>2</sub>O. The coupling of the two cycles formed a novel and efficient aerobic sulfide oxidation system.

In conclusion, we have found a highly efficient catalytic system for the oxidation of different sulfides with air as oxidant and have provided a very mild method for the oxidation of sulfides without using any transition metal.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/i.tetlet.2013. 10.102. These data include MOL files and InChiKeys of the most important compounds described in this article.

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- Yang, S. H. Synlett 2009, 1351. General procedure for the oxidation of sulfides: 27. Dissolve PvHBr<sub>2</sub> (0.3 mmol) in water (1 ml). Transfer the solution into a 100 ml round bottom flask with substrate (10 mmol), CH<sub>3</sub>CN (20 ml), and TBN (0.4 mmol). The reaction mixture was stirred at room temperature ( $\sim$ 25 °C) and air condition. Progress of the reaction was monitored by TLC and GC. Upon completion, the mixtures were removed and dissolved with CH<sub>2</sub>Cl<sub>2</sub>. Wash the mixtures with HCl (1  $\times$  10 ml), saturated sodium bicarbonate ((2  $\times$  10ml), and water (10 ml). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The yield was calculated on the basis of 10 mmol of substrate. Products are determined by GC, <sup>1</sup>H NMR, and <sup>13</sup>C NMR.