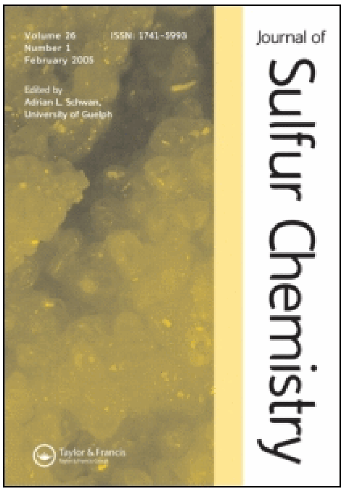

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$POCl_3$ as a catalytic activator for H_2O_2 activation in selective sulfide oxidation

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$POCl_3$ as a catalytic activator for H_2O_2 activation in selective sulfide oxidation

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Various types of sulfides are selectively oxidized to sulfoxides in excellent yields using 30% aqueous hydrogen peroxide as an oxidant in the presence of $POCl_3$ in ethanol at 50 °C. It is noteworthy that functional groups remain unaffected and only the sulfur atom is selectively oxidized.

Keywords: hydrogen peroxide; sulfides; sulfoxides; sulfoxidation reactions; activator

1. Introduction

Sulfoxidation reactions have significant importance in organic chemistry, medicinal chemistry, and drug metabolism (*1*). They have been utilized extensively in carbon–carbon bond formation reactions and as versatile building blocks in organic synthesis (*2, 3*). Selective oxidation of organic sulfides is very important from both industrial and green chemistry points of view as organosulfur compounds are a major source of environmental pollution (*4*).

Oxidation of sulfides is a very useful route for the preparation of sulfoxides. The popularity of this method is due to the availability of a wide variety of sulfides that can be utilized in the oxidation of sulfides to the corresponding sulfoxides. In view of the importance of sulfoxides, various oxidizing agents are used for this purpose (*5–10*).

However, in spite of their potential utility, many of these methods involve expensive reagents, longer reaction times, and unsatisfactory yields. Another major problem is over-oxidation to the sulfone. In recent years, the development of more economical and environmentally friendly conversion processes is gaining interest in the chemical community. Therefore, a need still exists for versatile, simple, and environmentally friendly processes whereby sulfoxides may be obtained under milder conditions.

Aqueous hydrogen peroxide is an ideal oxidant for liquid-phase reactions because it produces only water as a by-product, is safe to store and use, and is cheap and readily available. Many useful procedures involving aqueous hydrogen peroxide as terminal oxidant and a catalytic activator have

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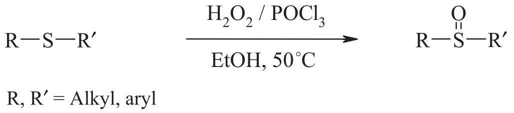


Scheme 1.

been developed to promote the oxidation of sulfides (*11*). The activator is essential for the success of the reaction as H_2O_2 by itself is a rather slow oxidizing agent.

As a part of our continued efforts to utilize hydrogen peroxide for useful synthetic transformations (*12*), here, we wish to report for the first time a simple, facile, and highly efficient methodology for the oxidation of sulfides to sulfoxides in excellent yields using H_2O_2 in the presence of $POCl_3$ (Scheme 1).

2. Results and discussion

Several solvents including acetonitrile, ethanol, acetone, and chloroform were investigated during the course of this study. The best results based on yields and reaction times were obtained using acetonitrile and ethanol.

Further efforts were then focused on optimizing the reaction conditions. The results, under different conditions, are summarized in Table 1.

As shown, a ratio of 1:2:0.5 sulfide/H_2O_2/$POCl_3$ was found to be optimum for the complete conversion of sulfides to sulfoxides.

Using the optimized reaction conditions, the reactions of various substituted sulfides including diaryl, dibenzyl, aryl benzyl, dialkyl, and heterocyclic sulfides were investigated (Table 2).

In all cases, the reactions resulted in 100% conversion of the sulfides. As shown in Table 2, sulfides bearing electron-donating and electron-withdrawing substituents gave the desired sulfoxides in excellent yields. Over-oxidation to sulfones was not observed. Another important feature of this procedure is the survival of a variety of functional groups such as nitro (Entry 2), ester (Entry 5), halides (Entries 4 and 8), C=C double bonds (Entry 14), and carbonyl groups (Entry 15), under the reaction conditions. Therefore, $POCl_3$ is an excellent activator for the highly chemoselective and fast oxidation of functionalized sulfides with 30% H_2O_2 under very mild conditions.

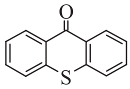
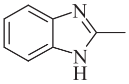
We have also monitored competitive oxidation of sulfides in the presence of alcohol, oxime, and acid functional groups. The results are shown in Scheme 2. These observations clearly suggest that this method can be applied for the chemoselective oxidation of sulfides in the presence of the above-mentioned functional groups in multifunctional molecules.

Table 1. Effect of increasing amount of $POCl_3$ on oxidation of benzyl phenyl sulfide, using H_2O_2.[a]

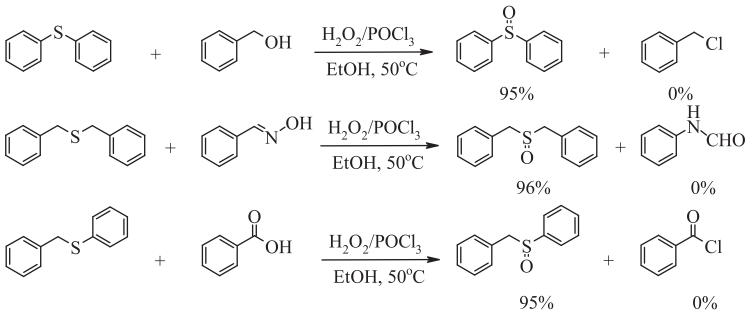
Entry	$POCl_3$ (mmol)	Yield (%)[b]
1	0	25
2	0.2	40
3	0.4	70
4	0.5	97

Notes: [a]Reaction conditions: the reactions were performed with benzyl phenyl sulfide (1 mmol), and H_2O_2 (2 mmol) for 14 min, at room temperature. [b]Isolated yields.

Table 2. Oxidation of sulfides to sulfoxides using the H_2O_2 (2 equiv)/$POCl_3$ (0.5 equiv) system in ethanol.[a]

Entry	R	R′	Time (min)	Yield (%)[b]	Ref.
1	C_6H_5	$C_6H_5CH_2$	14	97	(*13a*)
2	C_6H_5	4- $O_2NC_6H_4CH_2$	28	95	(*12a*)
3	C_6H_5	4-$MeC_6H_4CH_2$	9	97	(*13b*)
4	C_6H_5	4-$BrC_6H_4CH_2$	18	99	(*13c*)
5	C_6H_5	MeO_2CCH_2	45	92	(*13d*)
6	4-MeC_6H_4	$C_6H_5CH_2$	12	97	(*13e*)
7	4-MeC_6H_4	4-$MeC_6H_4CH_2$	11	95	(*14a*)
8	4-MeC_6H_4	4-$FC_6H_4CH_2$	20	90	(*13f*)
9	4-BrC_6H_4	$C_6H_5CH_2$	19	98	(*13c*)
10	4-$BrC_6H_4CH_2$	$C_6H_5CH_2$	10	97	(*12a*)
11	$C_6H_5CH_2$	$C_6H_5CH_2$	9	99	(*13g*)
12	C_6H_5	C_6H_5	14	98	(*13a*)
13	C_6H_5	CH_3	8	98	(*13g*)
14	Ph	$CH_2{=}CHCH_2$	10	97	(*13h*)
15			80	70[c]	(*14b*)
16		$C_6H_5CH_2$	40	95	(*14b*)
17	CH_3CH_2	CH_3CH_2	6	91	(*12i*)
18	$CH_3(CH_2)_2CH_2$	$CH_3(CH_2)_2CH_2$	11	95	(*12c*)

Notes: [a]The products were characterized by comparison of their spectroscopic and physical data with those reported in the literature. [b]Yields refer to pure isolated products. [c]1,4-Dioxane was used as the solvent.



Scheme 2. Reagents and conditions: molar ratio of substrates to $POCl_3$ to H_2O_2 (1:1:0.5:2), EtOH, 50 °C.

3. Conclusion

In summary, we have demonstrated that the $H_2O_2/POCl_3$ system is an excellent and convenient oxidizing reagent for the oxidation of sulfides to sulfoxides without any over-oxidation to sulfones. Under these conditions, functional groups remain unaffected and only the sulfur atom is selectively oxidized.

4. Experimental

4.1. *General procedure*

To a solution of sulfide (2 mmol) in EtOH (10 mL), H_2O_2 (30%, 4 mmol, 0.4 mL), and $POCl_3$ (1 mmol, 0.153 g) were added and the mixture was stirred at 50 °C for the indicated time (see Table 2). The progress of the reaction was monitored by TLC (eluent: n-hexane/ethyl acetate: 7/3). After disappearance of the sulfide, the reaction mixture was quenched by adding water (10 mL), extracted with ethyl acetate (4×5 mL) and the extract dried with anhydrous $MgSO_4$. The filtrate was evaporated and the corresponding sulfoxide was obtained as the only product.

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