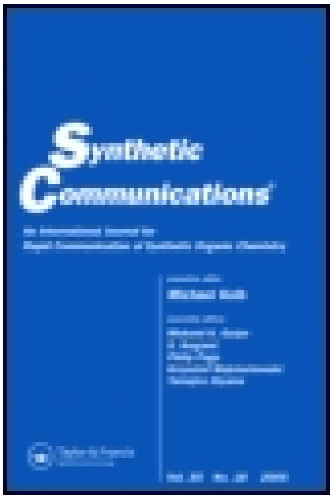

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VCl_3-Catalyzed Selective Oxidation of Sulfides to Sulfoxides Using H_2O_2 as Oxidant

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VCl_3-Catalyzed Selective Oxidation of Sulfides to Sulfoxides Using H_2O_2 as Oxidant

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Abstract: VCl_3 is an effective catalyst for the catalytic oxidation of sulfides to afford sulfoxides in good yields using hydrogen peroxide as an oxidant.

Keywords: Hydrogen peroxide, sulfides, sulfoxides, VCl_3

INTRODUCTION

A number of synthetic procedures are available for the oxidation of sulfides to chiral/achiral sulfoxides or sulfones.[1] The standard practice for carrying out such reactions involves oxidation of sulfides with various oxidizing reagents such as nitric acid,[2] $KMnO_4$,[3] m-chloroperbenzoic acid,[4] sodium periodate,[5] bromine,[6] nitrogentetraoxide,[7] oxaziridine,[8] benzeneseleninic peracid,[9] tert-butyl hydroperoxide,[10] sulfinyl peroxy compounds,[11] and 4-methylmorpholine *N*-oxide with osmium tetraoxide[12]. Most of these reagents perform unsatisfactorily for medium- to large-scale synthesis because of low effective oxygen content, leading to the formation of environmentally unfavorable by-products and high cost. Apart from these reagents, singlet oxygen or molecular oxygen combined with 2-methylpropanal and Co(II) complexes[13,14] have also been used. Aqueous hydrogen peroxide (30%) is an ideal oxidant in view of its high effective oxygen content (as high as 47%), cleanliness (it produces only water as a by-product), safety in

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storage and operation, and low cost of production and transportation.[15] Recently, Karimi et al. have reported highly efficient synthesis of sulfoxide with a recoverable silica-based tungstate interphase catalyst using hydrogen peroxide.[16] Selective synthesis of sulfoxides remains a challenging task and constitutes an active area of research on its own.

Vanadium trichloride and its complexes are gaining importance as mild Lewis acid catalysts to perform a plethora of organic transformations such as ring opening of epoxides, Biginelli condensation and deprotection of acetonide,[17] synthesis of bis-indoles and α-amino phosphonates,[18] and pinacol coupling.[19]

RESULTS AND DISCUSSION

In this communication, we disclose a simple, efficient sulfoxidation using 30% hydrogen peroxide as an oxidizing agent with a catalytic amount of VCl_3 (Scheme 1).

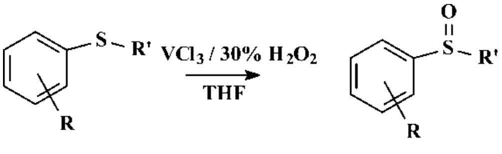
Several solvent systems were studied for the preparation of sulfoxides. The solvent has a pronounced effect on these reactions, in which water and dichloromethane afforded lower yields, whereas acetone and acetonitrile gave moderate yields, and methanol and tetrahydrofuran (THF) proved to be good solvents in selective oxidation of sulfides. The reaction was found to be complete within few minutes in THF at room temperature.

The controlled reaction conducted under identical conditions devoid of catalyst showed no oxidized product formation within the stipulated reaction time. Various structurally diverse sulfides underwent selective oxidation to give the corresponding sulfoxides with good to excellent yields with trace quantities of sulfones as confirmed by gas chromatography (GC) and ^{1}H NMR of the crude reaction mixture.

EXPERIMENTAL SECTION

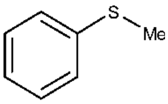
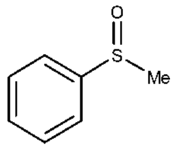
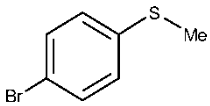
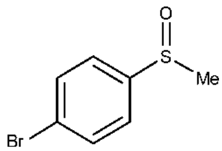
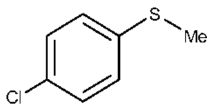
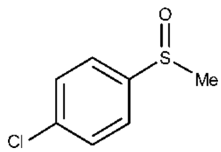
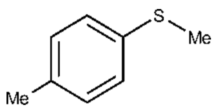
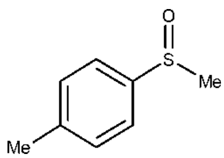
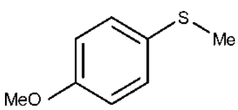
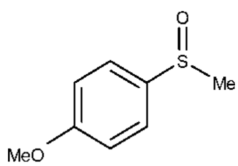
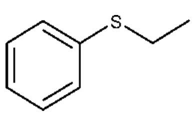
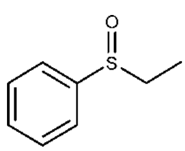
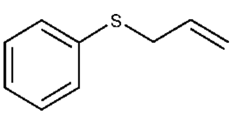
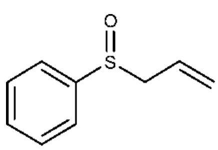
Typical Procedure for the Oxidation of Sulfides

To the stirred solution of the sulfide (124 mg, 1 mmol) and VCl_3 catalyst (6 mg, 5 mol%) in THF (5 ml), an aqueous solution of 30% (w/w) hydrogen



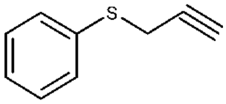
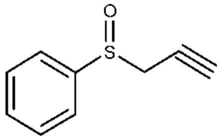
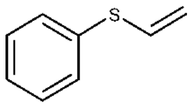
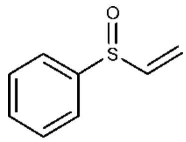
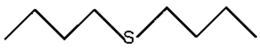
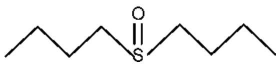
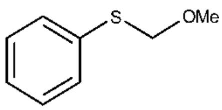
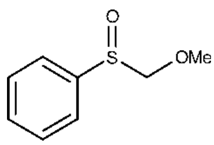
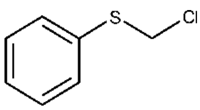
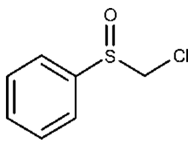
Scheme 1. VCl_3-catalyzed synthesis of sulfoxide.

Table 1. Vanadium(III)-catalyzed selective oxidation of sulfides to sulfoxides with 30% H_2O_2[a]

Entry	Substrate	Sulfoxide	Time (min)	Yield[b] (%)
1			5	98
2			5	95
3			5	93
4			8	96
5			10	94
6			10	92
7			10	95

(*continued*)

Table 1. Continued

Entry	Substrate	Sulfoxide	Time (min)	Yield[b] (%)
8			15	90
9			12	93
10			15	90
11			15	90
12			35	83

[a]Reaction conditions: sulfide (1 mmol), H_2O_2 (1 mmol), VCl_3 (5 mol%), and THF (4 mL).
[b]Isolated yields.

peroxide (0.1 ml, 1 mmol) was added dropwise at room temperature. After completion of the reaction (as monitored by thin-layer chromatography, TLC), the reaction mixture was extracted with ethyl acetate (2×10 ml). The organic phase was separated, dried over anhydrous sodium sulfate, and concentrated to afford the sulfoxide after silica-gel chromatography. All the products were characterized by ^{1}H NMR, mass, IR spectroscopy, and elemental analysis.

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