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RESEARCH ARTICLE

Oxidation of sulfides to sulfoxides with zirconium hydroxy chromate ($Zr_4(OH)_6(CrO_4)_5(H_2O)_2$)

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Various types of sulfides were converted to sulfoxide by zirconium hydroxy chromate in high yields and rates, under reflux conditions.

Keywords: Sulfide; Sulfoxide; Oxidation; Zirconium hydroxy chromate

1. Introduction

The increasing interest and applications of sulfoxides have stimulated investigations on new methodologies of sulfoxide synthesis. Organic sulfoxides are useful synthetic intermediates for the construction of various chemically and biologically active molecules. They often play an important role as therapeutic agents such as anti-ulcer (proton pump inhibitor) [1, 2], antibacterial, antifungal, anti-atherosclerotic [3, 4], anthelmintic [5, 6], antihypertensive [7], and cardiogenic agents [8, 9], as well as psychotonics [10, 11] and vasodilators [12].

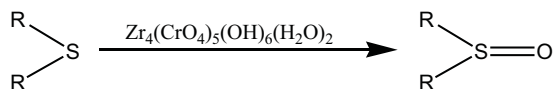
The oxidation of sulfides to sulfoxides is of significant importance in organic chemistry, both for fundamental research and for a wide range of applications. The synthesis of sulfoxides was reported for the first time by Märker [13] in 1865 and, since then, a number of methods have been developed for the conversion of sulfides into sulfoxides. Comprehensive reviews on the oxidation of sulfides to sulfoxides have been published in the past [14–16].

There are several reagents available for this key transformation [17–25]. Unfortunately, some of these reagents are not satisfactory as they may be either harmful or expensive, and a simple procedure is not easily available, because of the over-oxidation of sulfoxides to sulfones. Despite the careful control of the reaction temperature, reaction time, and the relative amounts of oxidants, it is difficult to avoid such over-oxidation completely [26, 27].

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As the sulfoxides are important for C–C bond formation and functional group transformations, the search for newer methods for the selective oxidation of sulfides to sulfoxides has continued.

In continuation of our study to explore new applications of zirconium hydroxide chromate [28, 29] ($Zr_4(OH)_6(CrO_4)_5(H_2O)_2$) (ZHC), we found that this compound is a useful, stable, and efficient reagent for oxidation of sulfide to their corresponding sulfoxides. (Scheme, Table)

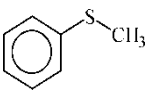
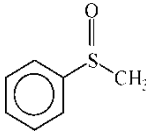
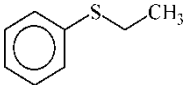
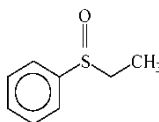
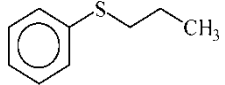
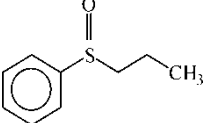
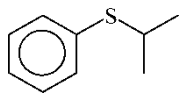
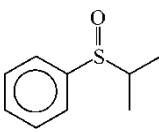
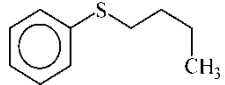
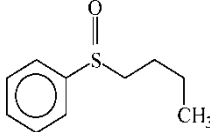
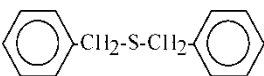
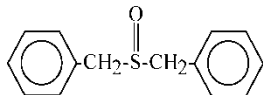


SCHEME 1

Zirconium hydroxide chromate, which is a red octahedral crystal, was prepared easily from the $K_2Cr_2O_7$, $Zr(NO_3)_4$, and CrO_3 [30–32].

As shown in table 1, in the presence of zirconium hydroxyl chromate (ZHC), various sulfides were easily converted into the corresponding sulfoxides in excellent yields (80–90%).

Table 1. Oxidation of sulfide to sulfoxide by ZHC under reflux condition.

Entry	Substrate	Product	Time (h)	Yield [†] %
1			3	90
2			3	90
3			3.5	88
4			4	90
5			4	85
6			2	90

(continued)

Table 1. Continued.

Entry	Substrate	Product	Time (h)	Yield [†] %
7			2	90
8			2	88
9			1.5	85
10			5	80
11			–	–
12			–	–

[†]Yields refer to isolated products. Structures are confirmed by ¹H-NMR, IR, mp/bp.

Phenyl alkyl sulfides (Entry 1–5) were efficiently converted to their corresponding sulfoxide in 85–90% yield. Benzyl phenyl sulfide and dibenzyl sulfide (Entry 6, 7) are oxidized to the corresponding sulfoxides in 90% yield.

In the oxidation of diphenyl sulfide to diphenyl sulfoxide, when there is an electron releasing group, the rate and yield of the reaction increased (Entry 8, 9). Bis(4-nitro phenyl) sulfide is oxidized to its corresponding sulfoxide taking a longer time with 80% yield. It is noteworthy that aliphatic sulfides (Entry 11, 12) not oxidized to the corresponding sulfoxides under these conditions may be because of the presence of bulky alkyl groups in the molecule and the lack of resonance that does exist between sulfur and aromatic rings in aromatic sulfides.

In conclusion, mild reaction conditions, high reaction rates, and high yields, deserve to be mentioned for the present procedure and make it a useful method for the preparation of various sulfoxides without requiring a large amount of the oxidant. Zirconium hydroxyl chromate is used as a stable and cheap reagent with a facile preparation.

2. Experiment

All products are known compounds and were identified by comparison of their physical and spectral data with those of authentic samples. IR spectral were recorded as neat films or as KBr

pellets on a Shimadzu model 8300 FT-IR spectrophotometer. $^1\text{H-NMR}$ spectra were recorded on a Bruker DPX-100 instrument with CDCl_3 as solvent and Me_4Si as an internal standard.

3. Typical procedure for oxidation sulfides to sulfoxides

To a solution of sulfide (1 mmol) in CH_3CN (5 mL) was added $(\text{Zr}_4(\text{OH})_6(\text{CrO}_4)_5(\text{H}_2\text{O})_2)$ (1–1.5 mmol). The resulting mixture was stirred at reflux. The progress of the reaction was monitored by TLC. After completion of the reaction, silica gel (1 g) was added to the mixture and the solvent was evaporated under reduced pressure. The resulting material was added on silica gel pad (3 cm thick) and was washed with *n*-hexane/ethyl acetate (5:1, 200 mL). The filtrate was concentrated to afford the desired product in excellent yield.

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References

- [1] S. Okabe, K. Shimosako. *J. Physiol. Pharmacol.*, **52**, 639 (2001).
- [2] C.M. Spencer, D. Faulds. *Drugs.*, **60**, 321 (2000).
- [3] M. Sovova, P. Sova. *Ceska Slov. Farm.*, **52**, 82 (2003).
- [4] M.A. Adetumjbi, B.H. Lau. *Med. Hypotheses.*, **12**, 222 (2000).
- [5] G. Merino, A.J. Molina, J.L. Garcia, M.M. Pulido, J.G. Prieto, A.I. Alvarez. *J. Pharm. Pharmacol.*, **55**, 757 (2003).
- [6] M.T. Teruel, A.E. Felipe, H.D. Solana, J.M. Sallovitz, C.E. Lanusse. *Vet. Hum. Toxicol.*, **45**, 131 (2003).
- [7] B. Kotelanski, R.J. Grozmann, J.N. Cohn. *Clin. Pharmacol. Ther.*, **14**, 427 (1973).
- [8] W.J. Parsons, V. Ramkumar, G.L. Stiles. *Mol. Pharmacol.*, **34**, 37 (1988).
- [9] R. Schmied, G.X. Wang, M. Korth. *Circ. Res.*, **68**, 597 (1991).
- [10] U.A. Zifko, M. Rupp, S. Schwarz, H.T. Zipko, E.M. Maida. *J. Neurol.*, **249**, 983 (2002).
- [11] A.V. Nieves, A.E. Lang. *Clin. Neuropharmacol.*, **25**, 111 (2002).
- [12] S. Padmanabhan, R.C. Lavin, G.J. Durant. *Tetrahedron: Asymmetry*, **11**, 3455 (2000).
- [13] C. Marcker. *Ann.*, **136**, 75 (1865).
- [14] M. Hudlicky. *Oxidations in Organic Chemistry, American Chemical Society Monograph 186*; American Chemical Society, Washington, DC (1990), Chapter 1 and 3.
- [15] K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski. *Tetrahedron*, **61**, 8315 (2005).
- [16] P. Kowalski, K. Mitka, K. Ossowska, Z. Kolarska. *Tetrahedron.*, **61**, 1933 (2005).
- [17] E. Block. *Reaction of Organosulfur Compound*, Academic Press, New York (1978).
- [18] H. Firouzabadi, N. Iranpoor, M.A. Zolfigol. *Synth. Commun.*, **28**, 377 (1998).
- [19] K.S. Ravikumar, J.P. Begue, D.B. Delpon. *Tetrahedron Lett.*, **39**, 3141 (1998).
- [20] M. Madesclaire. *Tetrahedron*, **42**, 5459 (1986).
- [21] T.K. Ganesan, S. Rajagopal, J.B. Bharathy. *Tetrahedron*, **56**, 5885 (2000).
- [22] G.J. Quallich, J.W. Lackey. *Tetrahedron Lett.*, **31**, 3685 (1990).
- [23] J. Brinksma, R. Crois, B.L. Feringa, M.I. Donnoli, C. Rosini. *Tetrahedron Lett.*, **42**, 4049 (2001).
- [24] H. Firouzabadi, M. Seddighi. *Synth. Commun.*, **21**, 211 (1991).
- [25] T. Durst. In *Comprehensive Organic Chemistry*, Barton, D., Ollis, W.D. (Eds.), Vol. 3, Pergamon: Oxford, (1979).
- [26] W.L. Xu, Y.Z. Li, Q.S. Zhang, H.S. Zhu. *Synthesis.*, **2**, 227 (2004).
- [27] T. Donohoe. *J. Oxidation and Reduction in Organic Synthesis*, Oxford University Press, New York (2000).
- [28] M. Rahimizadeh, M. Gholizadeh, H. Hassani, M. Bakavoli. *J. Chem. Res.*, **1**, 39 (2006).
- [29] M. Rahimizadeh, H. Hassani, M. Bakavoli, M. Gholizadeh. *Bull. Korean Chem. Soc.*, **1872**, 11 (2005).
- [30] G. Lundgren. *Arkiv Kemi*, **13**, 59 (1958).
- [31] G. Lundgren. *Svensk Kem. Tidskr.*, **71**, 200 (1959).
- [32] G. Lundgren. Chemical Abstract; 6726b (1959).