

Communications

Rapid and Efficient Deoxygenation of Sulfoxides with NbCl₅/NaI System

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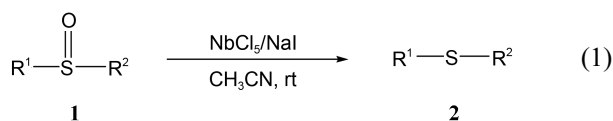
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The deoxygenation of sulfoxides to the corresponding sulfides is an important reaction that has found utility in organic synthesis and in biochemical reactions.¹ Accordingly, a good number of methods have been developed for the reduction of sulfoxides to the corresponding sulfides.² However, they often suffer from serious disadvantages, such as functional group incompatibility, difficult work-up procedures, harsh reaction conditions, or not readily available reagents. Further some of these methods are associated with limitations regarding low yields and prolonged reaction times. Therefore, the search for a new and efficient method for the deoxygenation of sulfoxides is still a worthwhile goal. Particularly much effort has been devoted to the development of milder conditions where the presence of various sensitive and reducible functional groups can be tolerated. The use of low valent oxophilic d-block metals (Zr, Ti, W, Mo) have become important in deoxygenation of various types of organic substrates.³ In this regard, deoxygenations of epoxides, sulfoxides and amine *N*-oxides are readily performed with low valent niobium generated by reacting NbCl₅ with Zn.⁴ We envisaged that NbCl₅/NaI system can be an efficient reducing agent for the reduction of sulfoxides to sulfides.

More recently, NbCl₅ has been well explored as a Lewis acid in promoting various organic transformations.⁵ Comparing with other Lewis acid, niobium(V) chloride has some advantages such as ease of handling, moisture stability, and good solubility in many organic solvents. We have investigated the reactions of NbCl₅/NaI system with various sulfoxides and found that they can be rapidly reduced to the corresponding sulfides in high yields (eq. 1). As a part of our



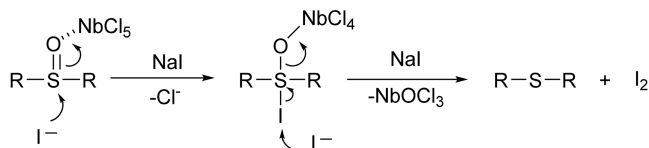
ongoing research work towards the development of the low-valent metal reagents for various transformations,⁶ we report here an efficient and chemoselective method for deoxygenation of sulfoxides **1** to the corresponding sulfides **2** with

NbCl₅/NaI system at room temperature. Metal-metal salt binary systems have long been used as reducing agents for many functional groups.⁷ In this communication, the use of the NbCl₅/NaI system is reported for the selective reduction of sulfoxides to sulfides in high yields under mild conditions. The new reducing system was generated by the addition of sodium iodide to a stirred solution of niobium pentachloride in CH₃CN.⁸ In comparison with other procedures, NbCl₅/NaI system reduces sulfoxides more rapidly (5 min) in higher yields (88-96%) and showed a good chemoselectivity. Some control experiments revealed that sulfoxides could not be deoxygenated by NbCl₅ alone under the present condition and starting materials were recovered unchanged. The optimal molar ratio of sulfoxide to niobium pentachloride to sodium iodide (1:2:3) is found to be ideal for the complete conversion of sulfoxide **1** into sulfide **2** in terms of yield and reaction time. And CH₃CN has been found to be the most suitable solvent for the reaction. In order to assess the scope and limitations of this reagent system, the reaction was studied with various sulfoxides

Table 1. Deoxygenation of sulfoxides with NbCl₅/NaI system

Entry	R ¹	R ²	Products	Time (min)	Yield (%) ^{a,b}
1	Ph	Ph	PhSPh	5	92
2	Ph	CH ₃	PhSCH ₃	5	96
3	4-BrC ₆ H ₄	CH ₃	4-BrC ₆ H ₄ SCH ₃	5	91
4	4-BrC ₆ H ₄	4-BrC ₆ H ₄	(4-ClC ₆ H ₄) ₂ S	5	94
5	4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	(4-CH ₃ OC ₆ H ₄) ₂ S	5	93
6	4-CHOC ₆ H ₄	CH ₃	4-CHOC ₆ H ₄ SCH ₃	5	95
7	Ph	CH=CH ₂	PhSCH=CH ₂	5	88
8	4-CH ₃ C ₆ H ₄	CH ₃	4-CH ₃ C ₆ H ₄ SCH ₃	5	92
9	4-CH ₃ C ₆ H ₄	4-CH ₃ C ₆ H ₄	(4-CH ₃ C ₆ H ₄) ₂ S	5	94
10	Ph	CH ₂ CH ₃	PhSCH ₂ CH ₃	5	91
11	PhCH ₂	PhCH ₂	(PhCH ₂) ₂ S	5	90
12	PhCH ₂	Ph	PhCH ₂ SPh	5	89
13	nC ₄ H ₉	nC ₄ H ₉	(nC ₄ H ₉) ₂ S	5	93

^aIsolated yields. ^bThe products are commercially available and were characterized by comparison of their spectral data with authentic samples.



Scheme 1

bearing other potentially labile functional groups. As shown in Table 1, the methodology is equally applicable to dialkyl, diaryl, and aryl alkyl sulfoxides. The functional group tolerance of this method is evident from entries 3-7 which show that bromo, chloro, methoxy, aldehyde, and vinyl functionalities are unaffected under the reaction conditions. Thus we have been able to demonstrate the utility of easily accessible NbCl_5/NaI system as a useful reagent for effecting chemoselective deoxygenation of sulfoxides. Although the reaction mechanism is still unclear, it can be rationalized as the result of a two-stage process. A possible mechanism is shown in Scheme 1. In the first step, the coordination of niobium(V) chloride to the oxygen proceeds to make the attack of iodide anion feasible. The resultant iodinated species is in turn attacked by another iodide anion to give the deoxygenated sulfide and concomitantly I_2 . The notable advantages of this methodology are mild reaction condition, fast reaction time, high yields, and tolerance of some functional groups. The utility of NbCl_5/NaI system as a new reducing agent is also demonstrated by the high yields of dibenzyl sulfide (entry 11) and phenyl benzyl sulfide (entry 12) obtained after the reduction of the corresponding sulfoxides. Usually the sulfoxides which contain a benzyl group are difficult to reduce by other reagents.⁹

In conclusion, we believe that the present procedure using NbCl_5/NaI system will offer a useful and efficient alternative to the existing methods for reduction of sulfoxides to sulfides.

In addition, the mildness, and rapidity as well as excellent yields make the present deoxygenation method highly practical for reduction of various sulfoxides.

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References

- (a) Carreno, M. C. *Chem. Rev.* **1995**, 95, 1717. (b) Solladie, G. *Synthesis* **1981**, 185.
- (a) For an earlier review, see: Madesclaire, M. *Tetrahedron* **1988**, 44, 6537. (b) Drabowicz, J.; Togo, H.; Mikolajczyk, M.; Oae, S. *Org. Prep. Proc. Int.* **1984**, 16, 171. (c) Schmizu, M.; Shibuya, K.; Hayakawa, R. *Synlett* **2000**, 1437. (d) Khurana, J. M. *Tetrahedron Lett.* **1998**, 39, 3829. (e) Yadav, J. S.; Reddy, B. V. S.; Srinivas, C.; Srihari, P. *Synlett* **2001**, 854. (f) Balicki, R. *Synthesis* **1991**, 155. (g) Miller, S. J.; Collier, T. R.; Wu, W. *Tetrahedron Lett.* **2000**, 41, 3781. (h) Balicki, R. *Synthesis* **1991**, 155. (i) Firouzabadi, H.; Iranpoor, N.; Jafarpour, M. *J. Sulfur Chem.* **2005**, 26, 313. (j) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Synthesis* **1979**, 61. (k) Bahrami, K.; Khodaei, M. M.; Karimi, A. *Synthesis* **2008**, 2543.
- (a) Cintas, D. *Activated Metals in Organic Synthesis*; CRC: Boca Raton, 1993. (b) Balicki, R. *Synthesis* **1991**, 155. (c) Drabowicz, J.; Mikorajczyk, M. *Synthesis* **1976**, 527.
- Oh, K. S.; William, E. K. *Tetrahedron* **2009**, 65, 2966.
- (a) Yadav, J. S.; Ganganna, B.; Bhunia, D. C.; Srihari, P. *Tetrahedron Lett.* **2009**, 50, 4318. (b) Wang, R.; Li, B. G.; Huang, T. K.; Shi, L.; Lu, X. X. *Tetrahedron Lett.* **2007**, 48, 2071. (c) Ravikumar, P. C.; Yao, L. H.; Fleming, F. F. *J. Org. Chem.* **2009**, 74, 7294. (d) Hou, J. T.; Liu, Y. H.; Zhang, Z. H. *J. Heterocycl. Chem.* **2010**, 47, 703.
- (a) Yoo, B. W.; Choi, K. H.; Lee, S. J.; Yoon, C. M.; Kim, S. H.; Kim, J. H. *Synth. Commun.* **2002**, 32, 63. (b) Yoo, B. W.; Lee, S. J.; Yoo, B. S.; Choi, K. I.; Kim, J. H. *Synth. Commun.* **2002**, 32, 2489. (c) Yoo, B. W.; Choi, K. H.; Kim, D. Y.; Choi, K. I.; Kim, J. H. *Synth. Commun.* **2003**, 33, 53. (d) Yoo, B. W.; Park, M. C.; Shin, J. I. *Bull. Korean Chem. Soc.* **2009**, 30, 1927. (e) Yoo, B. W.; Kim, J. H.; Yang, M. H. *Bull. Korean Chem. Soc.* **2010**, 31, 791. (f) Yoo, B. W.; Kim, S. H.; Kim, J. H. *Bull. Korean Chem. Soc.* **2010**, 31, 2757.
- (a) Sarmah, B. K.; Barua, N. C. *Tetrahedron* **1991**, 47, 8587. (b) Bezbarua, M. S.; Bez, G.; Barua, N. C. *Chem. Lett.* **1999**, 325. (c) Wang, W. B.; Shi, L. L.; Huang, Y. Z. *Tetrahedron Lett.* **1990**, 31, 1185. (d) Barua, M.; Boruah, A.; Prajapati, D.; Sandhu, J. S. *Tetrahedron Lett.* **1996**, 37, 4559. (e) B. Rama, R.; Gitali, D.; Yoofisaca, S. N.; Anil, K. S. *Synlett* **2005**, 358.
- A typical procedure for the deoxygenation of sulfoxides is as follows: To a solution of niobium pentachloride (540 mg, 2.0 mmol), diphenylsulfoxide (202 mg, 1.0 mmol) in CH_3CN (5 mL) were added sodium iodide (450 mg, 3.0 mmol). The mixture was stirred at room temperature and TLC analysis showed the substrate is completely deoxygenated within 5 min. After completion of the reaction, the reaction mixture was diluted with water and extracted with ethylacetate. The combined organic extracts were washed successively with 10% aq $\text{Na}_2\text{S}_2\text{O}_3$ (20 mL) and H_2O (20 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane:ethyl acetate = 2:1) to afford diphenylsulfide (171 mg, 92%).
- (a) Alper, H.; Kenney, E. C. H. *Tetrahedron Lett.* **1970**, 11, 53. (b) Chasar, D. W. *J. Org. Chem.* **1971**, 36, 613.