

Rapid and Mild Deoxygenation of Sulfoxides with MoCl₅/Gallium System under Ultrasonication

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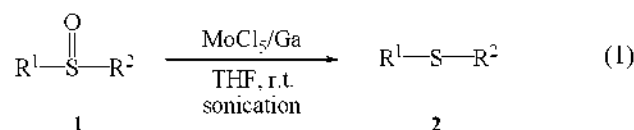
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The deoxygenation of sulfoxides to the corresponding sulfides is a valuable transformation that has found considerable utility in organic synthesis and in biochemical reactions. Accordingly, a good number of methodologies have been developed for the reduction of sulfoxides to sulfides.¹ However, many of these transformations often suffer from serious disadvantages, such as functional group incompatibility, difficult work-up procedures, or harsh reaction conditions. Further some of these methods are associated with limitations regarding low yields and long reaction times. Therefore, there still exists a search for new improved methods. 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 have become important in deoxygenation of various types of organic substrates.² In this regard, deoxygenations of sulfoxides and oximes are readily performed with low valent molybdenum generated by reacting MoCl₅ with either NaI, or Zn.³ We have investigated the reactions of MoCl₅/Ga system with various sulfoxides and found that they can be rapidly reduced to the corresponding sulfides in high yields (eq. (1)). In continuation of our efforts towards the development of the low-valent metal reagents for organic transformations,⁴ we wish to report a mild and efficient procedure for deoxygenation of sulfoxides **1** to the corresponding sulfides **2** with MoCl₅/Ga system at room temperature. Metal-metal salt



binary systems have long been used as reducing agents for many functional groups.⁵ In this communication, the use of the MoCl₅/Ga system is reported for the selective deoxygenation of sulfoxides to sulfides under mild conditions. Recently we have reported that TiCl₄/In or Cp₂TiCl₂/In could be used for the deoxygenation of various sulfoxides.⁶ The new reducing system was generated by the addition of gallium powder to a stirred solution of molybdenum pentachloride in THF under sonication.⁷ In comparison with other procedures, MoCl₅/Ga system reduces sulfoxides more rapidly (10 ~ 20 min) in high yields (85 ~ 95%) and showed a good chemoselectivity. A control experiment was carried out using sulfoxides with MoCl₅ alone, but without gallium metal under the present condition does not yield any reduced product and the starting material was recovered unchanged. Without ultrasonication⁸ the reaction was not complete. Thus, ultrasonic irradiation is necessary to accelerate the reaction. The optimum molar ratio of sulfoxide to molybdenum pentachloride to gallium (1 : 2 : 4) is found to be ideal for the complete conversion of sulfoxide **1** into sulfide **2** in terms of yield and reaction time. In order to assess the scope and limitations of this reagent system, the

Table 1. Deoxygenation of sulfoxides to sulfides with MoCl₅/Ga system

Entry	R ¹	R ²	Products	Time (min)	Yield (%) ^{a,b}
1	Ph	Ph	PhSPh	10	92
2	Ph	CH ₃	PhSCH ₃	10	90
3	4-BrC ₆ H ₄	CH ₃	4-BrC ₆ H ₄ SCH ₃	15	89
4	4-ClC ₆ H ₄	4-ClC ₆ H ₄	(4-ClC ₆ H ₄) ₂ S	20	88
5	4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	(4-CH ₃ OC ₆ H ₄) ₂ S	20	92
6	4-CHOC ₆ H ₄	CH ₃	4-CHOC ₆ H ₄ SCH ₃	20	86
7	Ph	CH=CH ₂	PhSCH=CH ₂	20	85
8	4-CH ₃ C ₆ H ₄	CH ₃	4-CH ₃ C ₆ H ₄ SCH ₃	15	93
9	4-CH ₃ C ₆ H ₄	4-CH ₃ C ₆ H ₄	(4-CH ₃ C ₆ H ₄) ₂ S	20	91
10	PhCH ₂	PhCH ₂	(PhCH ₂) ₂ S	20	90
11	PhCH ₂	Ph	PhCH ₂ SPh	10	92
12	nC ₄ H ₉	nC ₄ H ₉	(nC ₄ H ₉) ₂ S	15	95

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

reaction was studied with various sulfoxides bearing other potentially labile functional groups. As shown in Table 1, the methodology is equally applicable to dialkyl, diaryl, and aryl alkyl sulfoxides under the optimized reaction conditions. The sulfoxides possessing bromo, chloro, methoxy, aldehyde, and alkene functionalities were chemoselectively reduced to the corresponding sulfides in high yields without affecting these groups (Table 1, entries 3 - 7). Thus we have been able to demonstrate the utility of easily accessible MoCl₅/Ga 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. In the first step, molybdenum(V) chloride is probably reduced by gallium to form low-valent molybdenum species, which, in the subsequent step, would reductively deoxygenate sulfoxides **1** to give the corresponding sulfides **2**. The reducing property exhibited by metal-metal salt combinations proceeds through transfer of one electron from the metal surface to the substrate. In such combinations elementary metal part needs to be more electropositive than the metal part of the salt. We believe that the present procedure using MoCl₅/Ga system proceeds through a single electron transfer (SET) process. The notable advantages of this methodology are mild reaction condition, fast reaction time, high yield, and tolerance of some functional groups. The utility of MoCl₅/Ga system as a new reducing agent is also demonstrated by the high yields of dibenzyl sulfide (entry 10) and phenyl benzyl sulfide (entry 11) obtained after the reduction of the corresponding sulfoxides. Usually the sulfoxides which contain a benzyl group are difficult to reduce by other reagents without cleavage of C-S bond.⁹

In conclusion, we believe that the present procedure using MoCl₅/Ga system will present a useful and efficient alternative to the existing methods for the deoxygenation of sulfoxides to sulfides. Further investigation of MoCl₅/Ga system as reducing agent in organic synthesis is currently in progress in our laboratory.

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- A typical procedure for the deoxygenation of sulfoxides is as follows: To a solution of molybdenum pentachloride (238 mg, 1.0 mmol), diphenylsulfide (101 mg, 0.5 mmol) in anhydrous THF (5 mL) were added gallium (230 mg, 2.0 mmol). The resulting mixture was stirred at room temperature under sonication and the progress of the reaction was followed by TLC. After completion of the reaction (10 min) the reaction was quenched with aq. NaOH (10%), and extracted with ether. The combined ethereal extracts were washed successively with brine (20 mL) and H₂O (20 mL). The organic layer was separated and dried over anhydrous Na₂SO₄. The ether was removed under reduced pressure and the obtained crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 2:1) to afford diphenylsulfide (86 mg, 92%). Selected spectral data: **Diphenylsulfide (entry 1)**: ¹H NMR (300 MHz, CDCl₃) δ 7.38 - 7.25 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 135.7, 131.1, 129.2, 127.1. **Di(*p*-anisole) sulfide (entry 5)**: ¹H NMR (300 MHz, CDCl₃) δ 6.84 - 7.28 (m, 8H), 3.79 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 162.2, 137.4, 127.3, 115.1, 55.9. **Methyl *p*-tolyl sulfide (entry 8)**: ¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, 2H, *J* = 11.1 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 2.70 (s, 3H), 2.41 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 134.9, 134.6, 129.6, 127.4, 20.9, 16.6. **Benzyl phenyl sulfide (entry 11)**: ¹H NMR (300 MHz, CDCl₃) δ 7.33 - 7.19 (m, 10H), 4.13 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 137.4, 136.3, 129.9, 128.8, 128.5, 127.5, 127.1, 126.4, 39.2. **Dibutylsulfide (entry 12)**: ¹H NMR (300 MHz, CDCl₃) δ 2.65 (t, 4H, *J* = 7.2 Hz), 1.71 (m, 4H), 1.55 (m, 4H), 1.04 (t, 6H, *J* = 7.2 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 32.0, 30.3, 22.2, 13.8.
- Sonication were carried out in BRANSONIC ultrasonic cleaner bath, which delivered a 47 kHz wave, with a fixed electrical power of 125 Watts.
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