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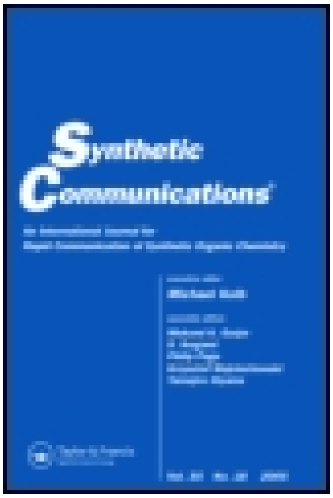

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Mild and Efficient Deoxygenation of Sulfoxides with a WCl_6/Indium System

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Abstract: Dialkyl, diaryl, and aryl alkyl sulfoxides can be rapidly converted to the corresponding sulfides with a WCl_6/In system in excellent yields under mild conditions.

Keywords: Deoxygenation, indium, sulfide, sulfoxides, WCl_6

The deoxygenation of sulfoxides to sulfides is a valuable transformation in the application of organosulfur compounds in organic synthesis. Particularly, sulfoxides deserve much attention as important chiral auxiliaries in asymmetric synthesis.[1] Accordingly, a good number of methodologies 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 workup procedures, harsh reaction conditions, or not readily available reagents. Further, some of these methods are associated with low yields and prolonged reaction times. Therefore, there still exists a need for new, improved methods based on easily accessible reagents and operationally simple procedures for the reduction of sulfoxides. The use of low-valent oxophilic d-block metals has become important in deoxygenation of various types of organic substrates.[3] In this regard, deoxygenations of sulfoxides and oximes are readily performed with low-valent tungsten generated by reacting WCl_6 with either NaI or Zn.[4] It is

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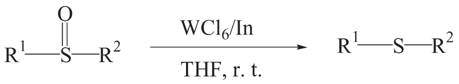
anticipated that a WCl_6/In system can be an efficient reducing agent for the reduction of sulfoxides to sulfides. We have investigated the reactions of the WCl_6/In system with various sulfoxides and found that they can be rapidly reduced to the corresponding sulfides in high yields [Eq. (1)].



$$R^1-\overset{\overset{O}{\|}}{S}-R^2 \xrightarrow[\text{THF, r. t.}]{WCl_6/In} R^1-S-R^2 \qquad (1)$$

1 **2**

Metal–metal salt binary systems have long been used as reducing agents for many functional groups.[5] In this communication, the use of the WCl_6/In system for the selective reduction of sulfoxides to sulfides in high yields under mild conditions is reported. Recently, we reported that $TiCl_4$/In or Cp_2TiCl_2/In could be used for the deoxygenation of various sulfoxides.[6] In comparison with other procedures, the WCl_6/In system reduces sulfoxides more rapidly (5 min) in higher yields (85–96%) and showed good chemoselectivity. Some control experiments revealed that sulfoxides could not be deoxygenated by WCl_6 or indium alone under the present condition, and starting materials were recovered unchanged. The new reducing system was generated by the addition of indium powder to a stirred solution of tungsten hexachloride in tetrahydrofuran (THF) under nitrogen. A 2:1 ratio of indium and WCl_6 was the best ratio in terms of yield and reaction time. The sulfoxides are prepared by oxidation of the corresponding sulfides with sodium metaperiodate in aqueous methanol.[7] All the compounds obtained showed IR, NMR, and mass spectral data compatible with the structure. To assess the scope and limitations of this reagent system, the reaction was studied with various sulfoxides bearing other potentially labile functional

Table 1. Reduction of sulfoxides with the WCl_6/In system

Entry	R^1	R^2	Products	Time (min)	Yield (%)[a]
1	Ph	Ph	PhSPh	5	92
2	Ph	CH_3	$PhSCH_3$	5	96
3	$4\text{-}BrC_6H_4$	CH_3	$4\text{-}BrC_6H_4SCH_3$	5	91
4	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	$(4\text{-}ClC_6H_4)_2S$	5	91
5	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	$(4\text{-}CH_3OC_6H_4)_2S$	5	93
6	$4\text{-}CHOC_6H_4$	CH_3	$4\text{-}CHOC_6H_4SCH_3$	5	95
7	$4\text{-}CH_3C_6H_4$	CH_3	$4\text{-}CH_3C_6H_4SCH_3$	5	89
8	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	$(4\text{-}CH_3C_6H_4)_2S$	5	89
9	Ph	CH_2CH_3	$PhSCH_2CH_3$	5	91
10	$PhCH_2$	$PhCH_2$	$(PhCH_2)_2S$	5	85
11	$PhCH_2$	Ph	$PhCH_2SPh$	5	87
12	nC_4H_9	nC_4H_9	$(nC_4H_9)_2S$	5	88

[a] Isolated yields.

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 3–6, which show that bromo, chloro, methoxy, and aldehyde functionalities are unaffected under the reaction conditions. Thus we have been able to demonstrate the utility of the easily accessible WCl_6/In 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, tungsten(VI) chloride is probably reduced by indium to form a low-valent tungsten species, which, in the subsequent step, reductively deoxygenates 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. We believe that the present reduction reaction using the WCl_6/In system proceeds through a SET (single-electron transfer) process. The method offers advantages such as mild reaction conditions, short reaction times, simple experimental operation, and tolerance of some functional groups. The utility of the WCl_6/In 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 that contain a benzyl group are difficult to reduce by other reagents.[8]

In conclusion, we believe that this procedure using the WCl_6/In system will present a useful and efficient alternative to the existing methods for reduction of sulfoxides to sulfides. Further investigation of the WCl_6/In system as a reducing agent in organic synthesis is currently in progress.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a FT-Bruker AF-300 (300 MHz for ^1H NMR; 75 MHz for ^{13}C NMR) using TMS as an internal standard. Infrared (IR) spectra were obtained on a Perkin-Elmer 16F PC FT-IR Shimadzu. Thin-layer chromatography (TLC) analysis was performed on silica-gel plates (Merck, 60 F-254). All products were purified by flash column chromatography using silica gel 60 (79–230 mesh, Merck).

General Procedure for the Reaction

A typical procedure for the deoxygenation of sulfoxides is as follows: Tungsten hexachloride (238 mg, 1.0 mmol) was added to a solution of indium (230 mg, 2.0 mmol) and diphenylsulfoxide (101 mg, 0.5 mmol) in anhyd. THF (1 mL). The mixture was stirred at room temperature, and the progress of the reaction was followed by TLC. After completion of the reaction (5 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 H_2O (20 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. The crude product was purified by silica-gel column chromatography (hexane–ethyl acetate = 1:1) to afford diphenylsulfide (86 mg, 92%).

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