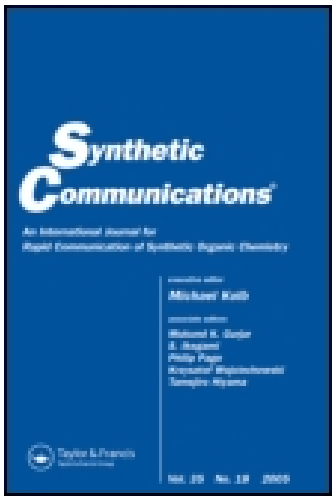

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MILD AND EFFICIENT REDUCTION OF SULFOXIDES TO SULFIDES WITH *BIS*-(CYCLOPENTADIENYL)TITANIUM(IV) DICHLORIDE–INDIUM SYSTEM

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ABSTRACT

Cp_2TiCl_2/In system was found to be a new reagent for reducing various sulfoxides to the corresponding sulfides in good yields under mild and neutral conditions.

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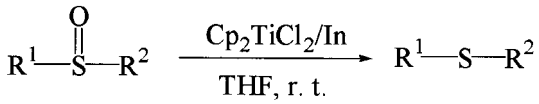
The chemical reactivity of Cp_2TiCl_2/M system (M = Na, Zn, Al, Mg, Sm) has been the subject of considerable interest and the reducing ability of these systems has been extensively studied.[1] It has recently been reported that Cp_2TiCl_2/samarium system is used as a reagent for reducing sulfoxides to sulfides.[1(d)] The reduction of sulfoxides to sulfides is a valuable transformation in the application of organosulfur compounds in organic synthesis and a number of methods have been developed for the reduction of sulfoxides.[2] We considered that Cp_2TiCl_2/In system can be an efficient reducing agent for the conversion of sulfoxides to sulfides. The application of process is highly desired in which protected thios are directly transformed into disulfides indium reagents in organic synthesis has attracted more and more interest in the last decade.[3] We have investigated the reactions of Cp_2TiCl_2/In system with various sulfoxides and found that they can be rapidly reduced to the corresponding sulfides in good yields (Eq. 1). The new reducing system was generated by the addition of indium powder to a stirred solution of *bis*(cyclopentadienyl)titanium(IV) dichloride in THF under nitrogen. Herein, we report the reduction of sulfoxides to sulfides by treatment with Cp_2TiCl_2/In under mild conditions. Some control experiments revealed that sulfoxides could not be reduced by Cp_2TiCl_2 or indium alone and were recovered unchanged.



1 **2** (1)

The reaction molar ratio of indium and Cp_2TiCl_2 is 1:2. If the molar ratio is changed to In:Cp_2TiCl_2 = 1:1, the reaction is not successful. In comparison with the Cp_2TiCl_2/Sm system, Cp_2TiCl_2/In system reduces sulfoxides more rapidly (10 min) in higher yields (73–93%) and showed a good chemoselectivity. The functional group tolerance of this method is evident from entries 3–6 which show that bromo, methoxy, aldehyde and vinyl are unaffected under the reaction conditions. All the compounds obtained showed IR, NMR and mass spectral data compatible with the structure. Sulfoxides as the substrate were prepared according to the literature procedure.[4] In order to assess the generality of the process, the reaction was studied with a variety of sulfoxides. As shown in Table 1, the methodology is applicable to aromatic, aliphatic and aralkyl sulfoxides. However, sulfones (entries 12 and 13) are not reduced under the reaction conditions. Thus, we have been able to demon-

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Table 1. Reduction of Sulfoxides with Cp_2TiCl_2/In System

Entry	R^1	R^2	Products	Reaction Time (min)	Yield (%)*
1	Ph	Ph	PhSPh	10	93
2	Ph	CH_3	$PhSCH_3$	10	85
3	4-BrC_6H_4	CH_3	4-$BrC_6H_4SCH_3$	10	90
4	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	(4-$CH_3OC_6H_4)_2S$	10	92
5	4-$CHOC_6H_4$	CH_3	4-$CHOC_6H_4SCH_3$	10	81
6	Ph	$CH{=}CH_2$	$PhSCH{=}CH_2$	10	73
7	4-$CH_3C_6H_4$	CH_3	4-$CH_3C_6H_4SCH_3$	10	90
8	Ph	CH_2CH_3	$PhSCH_2CH_3$	10	80
9	$PhCH_2$	$PhCH_2$	$(PhCH_2)_2S$	10	83
10	$PhCH_2$	Ph	$PhCH_2SPh$	10	85
11	nC_4H_9	nC_4H_9	$(nC_4H_9)_2S$	10	82
12	$PhCH_2S(=O)_2Ph$			no reaction	
13	$PhS(=O)_2CH_2CH_3$			no reaction	

*Isolated yield.

strate the utility of easily accessible Cp_2TiCl_2/In system as a convenient reagent for effecting chemoselective deoxygenation of sulfoxides. Although the role of *bis*(cyclopentadienyl)-titanium(IV) dichloride is still not clarified, it is assumed that reduction of titanium(IV) with indium provides low valent titanium,[5] which might be reducing the sulfoxides **1** to give the corresponding sulfides **2**. The notable advantages of this methodology are mild reaction condition, fast reaction time (10 min), simple operation, tolerance of some functional groups on the aromatic ring.

In conclusion, we believe this procedure using Cp_2TiCl_2/In system will present a useful and convenient alternative to the existing methods for reduction of sulfoxides to sulfides. Further investigations of Cp_2TiCl_2/In system as reducing agent in organic synthesis are currently in progress.

EXPERIMENTAL

Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl before use. ^{1}H NMR spectra were recorded on a FT-Bruker AF-300 (300 MHz for ^{1}H NMR; 75 MHz for ^{13}C NMR) using TMS as an internal standard. The solvent was $CDCl_3$ unless otherwise noted. IR spectra were obtained on a Perkin Elmer 16F PC FT-IR Shimadzu. GC-MS was

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recorded on a Hewlett-Packard 5890 GC. High resolution mass spectra (HRMS) were obtained on a Varian MATCH-50F instrument.

General Procedure for the Reaction

Bis(cyclopentadienyl)titanium(IV) dichloride (500 mg, 2.0 mmol), indium powder (115 mg, 1.0 mmol) and THF (5 mL) were mixed under nitrogen atmosphere and the resulting mixture was sirred at reflux for 30 min. A dark-red solution of the low-valent titanium-indium complex was obtained and cooled to room temperature. To this solution, diphenylsulfoxide (101 mg, 0.5 mmol) was added. The reaction mixture was stirred for 10 min at room temperature under nitrogen. The solvent was evaporated under reduced pressure and the residue was diluted with ether and filtered. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 6:1) to afford diphenylsulfide (87 mg, 93%).

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