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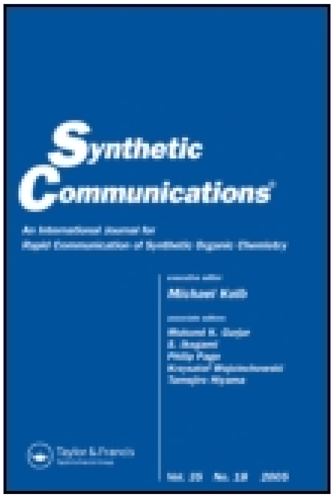

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Mild and Efficient Reduction of Sulfoxides to Sulfides with Titanium Tetrachloride-Indium System

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ABSTRACT

$TiCl_4$/In system was found to be a new reagent for reducing various sulfoxides to the corresponding sulfides in good yields under mild conditions.

Key Words: Sulfoxide; Sulfide; Titanium; Indium.

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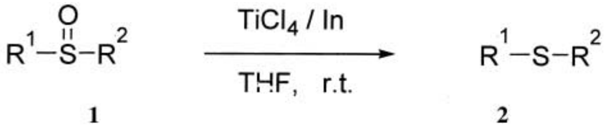
The chemical reactivity of $TiCl_4$/M system (M = Te, Mg, Zn, Sm) has been the subject of considerable interest and the reducing ability of these systems has been extensively studied.[1] It has recently been reported that $TiCl_4$/Sm system is used as a reagent for reducing sulfoxides to sulfides.[2] The reduction of sulfoxides to sulfides is a valuable transformation in the application of organosulfur compounds in organic synthesis and a good number of reagents have been developed for the reduction of sulfoxides to sulfides.[3] However, many of these procedures require harsh reaction conditions, and prolonged reaction times. There still exists a need for the development of new efficient and readily available reagents for this conversion. We considered that $TiCl_4$/In system can be an efficient reducing agent for the conversion of sulfoxides to sulfides. We have investigated the reactions of $TiCl_4$/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 titanium tetrachloride in THF under nitrogen. In continuation of our work on the applications of low-valent titanium reagent in various transformations,[4] herein we report a mild and efficient procedure for the deoxygenation of sulfoxides using $TiCl_4$/In system. Some control experiments revealed that sulfoxides could not be reduced by indium alone and were recovered unchanged.



$$R^1-\overset{O}{\overset{\|}{S}}-R^2 \xrightarrow[\text{THF, r.t.}]{TiCl_4 / In} R^1-S-R^2 \qquad (1)$$

1 **2**

In comparison with other procedures, $TiCl_4$/In system reduces sulfoxides more rapidly (10 min) in higher yields (84–95%) 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.[5] 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. Thus, we have been able to demonstrate the utility of easily accessible $TiCl_4$/In system as a convenient reagent for effecting

Table 1. Reduction of sulfoxides with $TiCl_4$/In system.[a]

Entry	R^1	R^2	Products	Reaction time (min)	Yield (%)[b]
1	Ph	Ph	PhSPh	10	91
2	Ph	CH_3	$PhSCH_3$	10	93
3	$4\text{-}BrC_6H_4$	CH_3	$4\text{-}BrC_6H_4SCH_3$	10	93
4	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	$(4\text{-}CH_3OC_6H_4)_2S$	10	95
5	$4\text{-}CHOC_6H_4$	CH_3	$4\text{-}CHOC_6H_4SCH_3$	10	91
6	Ph	$CH{=}CH_2$	$PhSCH{=}CH_2$	10	84
7	$4\text{-}CH_3C_6H_4$	CH_3	$4\text{-}CH_3C_6H_4SCH_3$	10	95
8	Ph	CH_2CH_3	$PhSCH_2CH_3$	10	87
9	$PhCH_2$	$PhCH_2$	$(PhCH_2)_2S$	10	89
10	$PhCH_2$	Ph	$PhCH_2SPh$	10	93
11	nC_4H_9	nC_4H_9	$(nC_4H_9)_2S$	10	85

[a] Mole ratio of sulfoxide:$TiCl_4$:Indium = 1:1:0.5.
[b] Isolated yield.

chemoselective deoxygenation of sulfoxides. Although the role of titanium tetrachloride is still not clarified, it is assumed that reduction of titanium(IV) with indium provides low valent titanium,[6] 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, simple operation, and tolerance of some functional groups on the aromatic ring. The utility of $TiCl_4$/In system as a new reducing agent is also demonstrated by the high yields of dibenzyl sulfide (Entry 9) and phenyl benzyl sulfide (Entry 10) obtained after the reduction of the corresponding sulfoxides. Usually the sulfoxides which contain a benzyl group are difficult to reduce by other reagents.[7]

In conclusion, we believe that this procedure using $TiCl_4$/In system will present a useful and convenient alternative to the existing methods for reduction of sulfoxides to sulfides. Further investigations of $TiCl_4$/In system as reducing agent in organic synthesis are currently in progress.

EXPERIMENTAL

Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl before use. ^1H 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 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

Indium powder (58 mg, 0.5 mmol), titanium tetrachloride (226 mg, 1.2 mmol) and THF (10 mL) were mixed under nitrogen atmosphere and the resulting mixture was stirred at room temperature for 1 h. A dark-blue solution of the low-valent titanium–indium complex was obtained and cooled to room temperature. To this solution, diphenylsulfoxide (202 mg, 1.0 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 (169 mg, 91%).

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REFERENCES

1. (a) Suzuki, H.; Manabe, H.; Enokiya, R.; Hanazaki, Y. Chem. Lett. **1986**, 1339; (b) Periasamy, M.; Reddy, M.R.; Kanth, J.V.B. Tetrahedron Lett. **1996**, *37*, 4767; (c) Li, T.; Cui, W.; Liu, J.; Zhao, J.; Wang, Z. J. Chem. Soc., Chem. Commun. **2000**, 139; (d) Zhou, L.; Zhang, Y. Synth. Commun. **1999**, *29*, 533; (e) Zhou, L.; Zhang, Y. Tetrahedron **2000**, *56*, 2953.
2. Wang, J.Q.; Zhang, Y.M. Synth. Commun. **1995**, *25*, 3545.
3. (a) See for a review: Madesclaire, M. Tetrahedron **1988**, *21*, 6537; (b) See for an earlier review: 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) Firouzabadi, H.; Karimi, B. Synthesis **1999**, 500.

4. (a) Yoo, B.W.; Choi, K.H.; Ko, J.J.; Nam, G.S.; Chang, K.Y.; Choi, K.I.; Kim, J.H. Bull. Kor. Chem. Soc. **2001**, *22*, 537; (b) Yoo, B.W.; Choi, K.H.; Lee, S.J.; Yoon, C.M.; Kim, S.H.; Kim, J.H. Synth. Commun. *in press*; (c) Yoo, B.W.; Lee, S.J.; Yoo, B.S.; Choi, K.I.; Kim, J.H. Synth. Commun. *in press*.
5. (a) Baugarten, H.E., Ed. *Organic Synthesis*; John Wiley and Sons: New York, London, Sydney, Toronto, 1973; Coll, Vol. 5, p. 791; (b) Shriner, R.L.; Struk, H.C.; Jorison, W.J. J. Am. Chem. Soc. **1930**, *52*, 2060.
6. Davies, S.G.; Thomas, S.E. Synthesis **1984**, 1027.
7. (a) Alper, H.; Kenney, E.C.H. Tetrahedron Lett. **1970**, 53; (b) Chasar, D.W. J. Org. Chem. **1971**, *36*, 613.

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