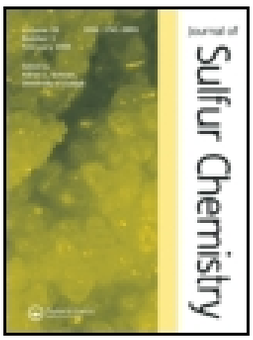

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Rapid and efficient deoxygenation of sulfoxides to sulfides with tantalum(V) chloride/sodium iodide system

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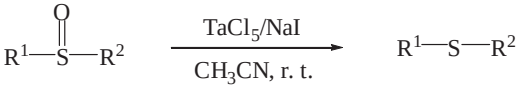
ABSTRACT

$TaCl_5$/NaI system converts a wide range of sulfoxides to the corresponding sulfides in high yields with short reaction times, under mild conditions. It is worth mentioning that this protocol is chemoselective and tolerates various functional groups (such as –Br, –Cl, $–OCH_3$, –CHO, and $–NO_2$) and double bond.



R^1, R^2 = Aryl and Alkyl

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Deoxygenation; sulfoxide; sulfide; tantalum(V) chloride; sodium iodide

1. Introduction

The deoxygenation of sulfoxides to sulfides constitutes a process of importance in both organic synthesis and biochemistry [1]. Sulfoxides are important intermediates in a variety of synthetic transformations, especially as chiral auxiliaries in asymmetric synthesis. After the asymmetric transformation, the sulfoxide moiety is removed from the target molecule through deoxygenation followed by desulfidation [2–5]. There are many available methods that can be used to convert sulfoxides to their corresponding sulfides [6–18]. However, most of these methods often suffer from drawbacks, including functional group incompatibility, long reaction times, harsh reaction conditions or complex experimental procedures. For these reasons, the search for mild and efficient methods based on easily accessible reagents and operationally simple procedures to overcome the limitations remains an important challenge in organic synthesis. The uses of oxophilic d-block metals have become important in deoxygenation of various types of organic molecules [19]. In this regard, the chemistry of $TaCl_5$ is one of the current interest in organic synthesis and has been extensively studied [20–24]. Fortunately, tantalum(V) compounds generally have low toxicity and are not considered particularly poisonous [25]. Attracted by the strong oxophilic character of $TaCl_5$, we decided to investigate its reactivity with sulfoxides. As a

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result we are gratified to report herein that the $TaCl_5$/NaI system efficiently deoxygenates various sulfoxides in high yields under mild conditions.

2. Results and discussion

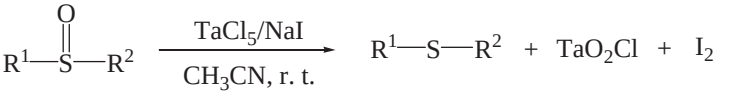
We have investigated the reactions of the $TaCl_5$/NaI system with a broad range of sulfoxides. All the reactions proceeded almost instantaneously upon addition of sodium iodide to a suspension of $TaCl_5$ and sulfoxide in acetonitrile at room temperature and the corresponding sulfides were obtained in high yields. We have found that the optimized molar ratio of the substrate with respect to $TaCl_5$ and NaI was 1/0.5/2 which under mild conditions the reaction was completed in a short time (3–5 min). The route for the synthesis of sulfides is shown in Scheme 1.

To ensure the role of NaI, a control experiment was carried out with $TaCl_5$ in the absence of NaI under the present condition, which failed to yield any desired product. It is obvious that a combination of $TaCl_5$ and NaI is essential for the efficient reduction of sulfoxides. To evaluate the solvent effect, the deoxygenation of diphenyl sulfoxide was carried out using different organic solvents such as toluene, dichloromethane, methanol, tetrahydrofuran, and acetonitrile. Among the solvents that were examined, acetonitrile turned out to be the most suitable solvent for this transformation in terms of reaction time and yield.

In order to assess the generality and scope of this reagent system, we examined the deoxygenation of a variety of sulfoxides bearing other potentially labile functional groups. An inspection of the data in Table 1 shows that diaryl, dialkyl, and aryl alkyl sulfoxides are all reduced smoothly, giving sulfides in yields exceeding 89%. The isolated yield was independent of the nature of the substituents. Thus, high yields were observed for sulfoxides with either electron-withdrawing or electron-releasing substituents on the aromatic ring with no obvious preference on the reactivity. However, the attempted reduction of diphenyl sulfone resulted in the recovery of starting material, suggesting that the polarized nature of sulfoxides is critical for reactivity [26].

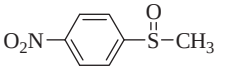
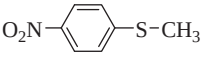
The functional group tolerance of this method is evident from entries 8–13, which show that the sulfoxides possessing bromo, chloro, methoxy, aldehyde, vinyl, and nitro functionalities are chemoselectively reduced to the corresponding sulfides without affecting these groups under the reaction conditions. Thus we have been able to demonstrate the utility of easily accessible $TaCl_5$/NaI system as a useful reagent for effecting chemoselective deoxygenation of sulfoxides.

A plausible mechanism for the reductive S–O bond cleavage of the sulfoxide can be rationalized as illustrated in Scheme 2. The reaction presumably proceeds via initial complexation of a sulfonyl oxygen with a Lewis acid, $TaCl_5$, which facilitates stepwise reduction of the sulfoxide. In the first step, the coordination of tantalum(IV) chloride to the oxygen



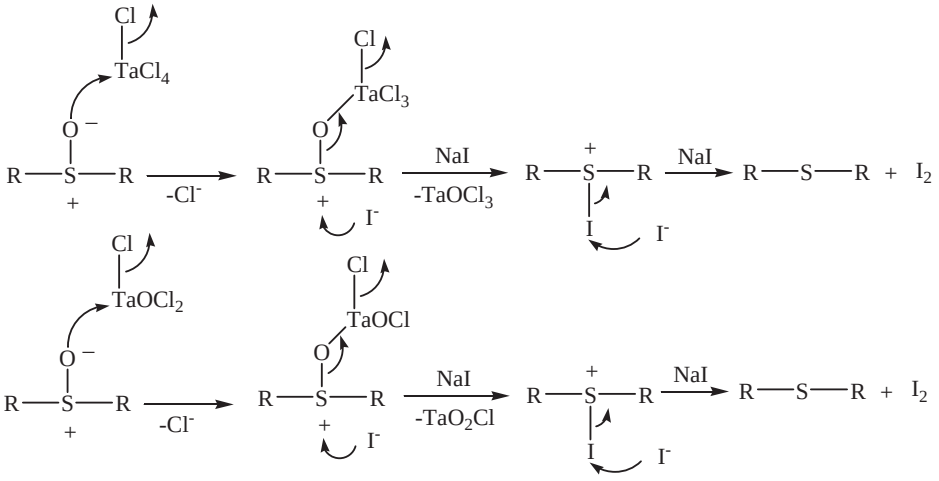
Scheme 1. Conversion of sulfoxides to their corresponding sulfides.

Table 1. Deoxygenation of various sulfoxides to sulfides using the TaCl5/NaI system.

Entry	R^1	R^2	Products	Time (min)	Yield (%)[a,b]
1	Ph	Ph	PhSPh	3	95
2	Ph	CH_3	$PhSCH_3$	3	96
3	nC_4H_9	nC_4H_9	$(nC_4H_9)_2S$	5	94
4	$4\text{-}CH_3C_6H_4$	$4CH_3C_6H_4$	$(4\text{-}CH_3C_6H_4)_2S$	3	93
5	$4\text{-}CH_3C_6H_4$	CH_3	$4\text{-}CH_3C_6H_4SCH_3$	3	94
6	$PhCH_2$	$PhCH_2$	$(PhCH_2)_2S$	5	96
7	$PhCH_2$	Ph	$PhCH_2SPh$	3	94
8	$4\text{-}BrC_6H_4$	CH_3	$4\text{-}BrC_6H_4SCH_3$	3	91
9	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	$(4\text{-}ClC_6H_4)_2S$	5	93
10	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	$(4\text{-}CH_3OC_6H_4)_2S$	5	92
11	$4\text{-}OHCC_6H_4$	CH_3	$4\text{-}OHCC_6H_4SCH_3$	5	90
12	Ph	$CH_2{=}CH$	$PhSCH{=}CH_2$	3	89
13				5	90

[a]Refers to isolated yields.

[b]All the products were characterized by comparison of their spectral data with authentic samples.



Scheme 2. Proposed mechanism for the deoxygenation of sulfoxide.

proceeds to make the attack of iodide anion feasible. In a subsequent step, the resultant iodinated species is in turn attacked by another iodide anion to give the deoxygenated sulfide and concomitantly I_2. The immediate development of a deep brown color was observed, which is consistent with the generation of molecular iodine in the reaction mixture. We have also found that half a molar equivalent of $TaCl_5$ and two molar equivalents of NaI were required to complete the reaction. On the basis of our observations, we have proposed a mechanism in which reduction of sulfoxides with $TaCl_5$ produces $TaOCl_3$, which would react with another equivalent of sulfoxide to give sulfide and TaO_2Cl.

The utility of the present protocol as a new reducing agent is also demonstrated by the high yields of dibenzyl sulfide (entry 6) and benzyl phenyl sulfide (entry 7) obtained after the reduction of the corresponding sulfoxides. Usually the sulfoxides which contain a benzyl group are not reduced or give very poor yields with other reducing agents and can undergo C–S bond cleavage reactions [27,28].

3. Conclusion

In conclusion, we believe that the present procedure will present a practical and useful alternative to the conventional methods for the deoxygenation of sulfoxides to sulfides. Further investigations are currently in progress to extend the scope of this methodology in our laboratory.

4. Experimental

4.1. General

The starting materials and solvents were purchased from commercial suppliers (Fluka and Sigma-Aldrich Chemical Companies) and used without further purification. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were determined on a FT-Bruker AF-300 NMR spectrometer in $CDCl_3$ using tetramethylsilane as internal standard. Chemical shifts were reported in ppm (δ) and coupling constants (J) in Hz. GC/MS measurements were carried out on a Shimadzu GC/MS-QP 1000. Thin-layer chromatography (TLC) analysis was performed on silica gel plates (Merck, 60 F-254). All products were purified by flash column chromatography on silica gel 60 (79-230 mesh, Merck) with ethyl acetate and hexane. ^{1}H and ^{13}C NMR spectra of the products agreed with the reported data.

4.2. General procedure

In a 10 mL round-bottom flask, to a solution of diphenylsulfoxide (202 mg, 1.0 mmol) in CH_3CN (4 mL), tantalum (IV) chloride (179 mg, 0.5 mmol) and sodium iodide (300 mg, 2.0 mmol) were added at room temperature. The mixture turned dark brown almost immediately and the progress of the reaction was followed by TLC. After completion of the reaction (3 min), the reaction mixture was diluted with water and then extracted with ethyl acetate. The combined organic extracts were washed successively with 10% aq $Na_2S_2O_3$ and H_2O. The organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified through silica gel column chromatography (hexane:ethyl acetate = 2:1) to afford diphenylsulfide (88 mg, 95%). All the products were characterized by comparison of their spectral data with those reported in the literature [29–31].

4.3. Spectroscopic data of products

Diphenyl sulfide (Table 1, *Entry 1*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42–7.39 (m, 4H), 7.38–7.34 (m, 3H), 7.33–7.26 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.7, 131.1, 129.2, 127.1. GC/MS (m/z): 186 (M^+).

Methyl phenyl sulfide (Table 1, *Entry 2*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17–7.15 (m, 5H), 2.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5, 128.8, 126.7, 125.0, 15.7. GC/MS (m/z): 124 (M^+).

Dibutyl sulfide (Table 1, *Entry 3*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.61–2.68 (m, 4H), 1.68–1.73 (m, 4H), 1.42–1.52 (m, 4H), 0.95 (t, 6H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.0, 30.4, 22.2, 13.8. GC/MS (m/z): 146 (M^+).

Di(4-methylphenyl) sulfide (Table 1, *Entry 4*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01–7.45 (m, 8H), 2.31 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.8, 132.8, 131.3, 129.8, 21.4. GC/MS (*m*/*z*): 214 (M^+).

Methyl 4-tolyl sulfide (Table 1, *Entry 5*): ^{1}H NMR (300 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.9, 134.6, 129.6, 127.4, 20.9, 16.6. GC/MS (*m*/*z*): 138 (M^+).

Dibenzyl sulfide (Table 1, *Entry 6*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.25 (m, 10H), 3.61(s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2, 129.2, 128.6, 127.2, 35.7. GC/MS (*m*/*z*): 214 (M^+).

Benzyl phenyl sulfide (Table 1, *Entry 7*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33–7.19 (m, 10H), 4.13 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.4, 136.3, 129.9, 128.8, 128.4, 127.8, 127.1, 125.4, 39.1. GC/MS (*m*/*z*): 200 (M^+).

Methyl 4-bromophenyl sulfide (Table 1, *Entry 8*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, 2H, J = 8.5 Hz), 7.12 (d, 2H, J = 8.6 Hz), 2.47 (3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5, 132.0, 128.9, 119.6, 15.0. GC/MS (*m*/*z*): 202 (M), 204 (M+2).

Di(4-chlorophenyl) sulfide (Table 1, *Entry 9*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.46 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.0, 132.9, 130.8, 129.7. GC/MS (*m*/*z*): 254 (M), 258 (M+2).

Di(4-anisole) sulfide (Table 1, *Entry 10*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.84–7.28 (m, 8H), 3.79 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2, 137.4, 127.3, 115.1, 55.9. GC/MS (*m*/*z*): 246 (M^+).

4-(Methylthio)benzaldehyde (Table 1, *Entry 11*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.93 (s, 1H), 7.78 (d, 2H, J = 8.4 Hz), 7.33 (d, 2H, J = 8.0 Hz), 2.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.0, 145.1, 133.2, 130.0, 127.1, 14.7. GC/MS (*m*/*z*): 152 (M^+).

Phenyl vinyl sulfide (Table 1, *Entry 12*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42–7.27 (m, 5H), 6.55 (dd, 1H, J = 15.7 Hz, J = 10.4 Hz), 5.39–5.33 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.2, 132.3, 129.6, 129.1, 125.6. 114.7. GC/MS (*m*/*z*): 136 (M^+).

Methyl 4-nitrophenyl sulfide (Table 1, *Entry 13*): ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, 2H, J = 8.9 Hz), 7.25 (d, 2H, J = 8.9 Hz), 2.52 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.1, 144.5, 124.9, 123.8, 14.7. GC/MS (*m*/*z*): 169 (M^+).

Disclosure statement

No potential conflict of interest was reported by the authors.

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