# Hypervalent Iodine(V)-Induced Asymmetric Oxidation of Sulfides to Sulfoxides Mediated by Reversed Micelles: Novel Nonmetallic Catalytic System

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Although several types of chiral hypervalent iodine reagents have been used for asymmetric induction, all of them have needed more than a stoichiometric amount of chiral reagents and have shown low enantioselectivities. The described new catalytic asymmetric oxidation using a hypervalent iodine(V) reagent, iodoxybenzene ($PhIO_2$), in a cationic reversed micellar system provides the first example of a catalytic asymmetric oxidation of sulfides to sulfoxides in high chemical yield with moderate to good enantioselectivity without the use of any transition-metal catalysts. The solubilization and activation of $PhIO_2$ by adding catalytic amounts of both cetyltrimethylammonium bromide (CTAB) and a chiral tartaric acid derivative were found to be indispensable for the enhancement of chemical and optical yields.

## Introduction

Hypervalent iodine reagents have been extensively used in organic syntheses due to their low toxicity, ready availability, and easy handling.[1] However, regarding asymmetric induction, especially that of sulfides to sulfoxides, several types of hypervalent iodine reagents have been examined with little success. These include reagents coordinated by chiral ligands or a chiral host compound such as carboxylic acids,[2a,c,g] sulfonic acids,[2f,i] alcohols,[2d] binaphthyl group,[2e] ethers,[2h,j,k] and $\beta$-cyclodextrin.[2b] The poor efficiency and practicality have been attributed to their low enantioselectivities and the necessity of more than a stoichiometric amount of chiral sources. As a result, hypervalent iodine reagents have normally been used merely as co-oxidants in transition-metal-catalyzed asymmetric oxidation reactions.[3] Therefore, the development of catalytic and enantioselective hypervalent iodine-induced oxidation of sulfides to sulfoxides has been an important area of organosulfur chemistry.

As a continuation of our studies on hypervalent iodine chemistry,[4] we recently reported quaternary ammonium salt catalyzed oxidation of sulfides to the corresponding sulfoxides in micellar and reversed micellar systems using iodosobenzene (PhI═O).[5] We were therefore curious whether placing PhI═O in an organized chiral surfactant medium, such as a micelle, could oxidize sulfides to sulfoxides stereoselectively. Several applications of micellar systems to stereoselective organic syntheses using chiral surfactants have been reported.[6] Among such examples, asymmetric oxidation reactions, to our knowledge, have only produced poor stereoselectivities (up to 15% ee).[7] Accordingly, the use of chiral quaternary ammonium salts such as *N*-[4-(trifluoromethyl)benzyl]-cinchoninium bromide and (−)-cetyldimethylphenylethylammonium bromide instead of CTAB were not at all effective for asymmetric induction in our recently developed micellar and reversed micellar systems.[5] We have

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(3) For the asymmetric oxidation of sulfides to sulfoxides, see: (a) Groves, J. T.; Viski, P. *J. Org. Chem.* **1990**, *55*, 3628−3634. (b) Halterman, R. L.; Jan, S.-T.; Nimmons, H. L. *Synlett* **1991**, 791−792. (c) Chiang, L.-C.; Konishi, K.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1992**, 254−256. (d) Naruta, Y.; Tani, F.; Maruyama, K. *Tetrahedron: Asymmetry* **1991**, *2*, 533−542. (e) Noda, K.; Hosoya, N.; Irie, R.; Yamashita, Y.; Katsuki, T. *Tetrahedron* **1994**, *32*, 9609−9618. (f) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S. *Chem. Commun.* **1996**, 931−932. (g) Kokubo, C.; Katsuki, T. *Tetrahedron* **1996**, *52*, 13895−13900. (h) Baird, C. P.; Rayner, C. M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1973−2003 and references therein.

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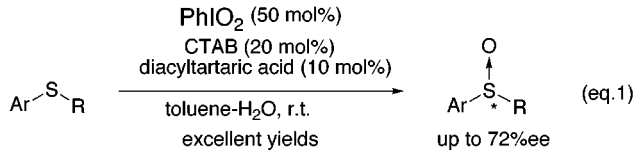
made subsequent improvements on this micellar system and now report a novel nonmetallic asymmetric oxidation reaction of sulfides to sulfoxides devoid of overoxidation to sulfones with moderate to good enantioselectivities (up to 72% ee)[8] using a hypervalent iodine(V) reagent, iodoxybenzene[9] ($PhIO_2$) (0.5 equiv), in toluene in the presence of catalytic amounts of cetyltrimethylammonium bromide (CTAB), water, and readily available chiral diacyltartaric acid (**3**) (eq 1).



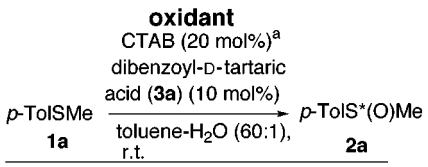

## Results and Discussion

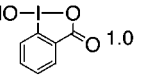
First, we examined whether a chiral additive could induce enantioselective oxidation of sulfides in our micellar systems. We found that in the presence of 10 mol % of dibenzoyl-D-tartaric acid (**3a**) and 20 mol % of CTAB (achiral quaternary ammonium salt) oxidation of methyl *p*-tolyl sulfide (**1a**) to methyl *p*-tolyl sulfoxide (**2a**) by PhI=O in 60:1 toluene−$H_2O$ proceeds in 80% yield with 30% ee. Hence, the next step was to enhance the enantioselectivity by altering oxidants, water content, and chiral sources.

We examined the asymmetric oxidation in CTAB reversed micelles using a variety of oxidants. Table 1 shows that among the hypervalent iodine reagents, 0.5 equiv of $PhIO_2$ was most effective for the asymmetric oxidation of **1a**.[10] Increasing the amount of $PhIO_2$ did not affect enantioselectivity at all but accelerated the reaction without yielding the corresponding sulfone (entries 3 and 4; Table 1). Similarly, increasing the equivalencies of CTAB and **3a** accelerated the reaction, but did not enhance its enantioselectivity.[11]

In contrast to iodine(III) or (V) reagents, other oxidants such as $H_2O_2$, cumene hydroperoxide, and sodium hypochlorite gave only poor enantiomeric excesses (entries 7−9; Table 1). In all cases, in the absence of CTAB the reaction did not proceed at all, indicating that the formation of the micellar system is essential for the sulfoxidation.

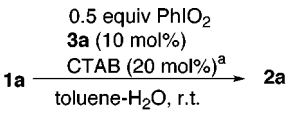
**Table 1**




| entry | oxidant | equiv | time (h) | yield (%) | ee (%) |
|---|---|---|---|---|---|
| 1 | PhIO | 1.0 | 2 | 80 | 30 |
| 2 | **$PhIO_2$** | **0.5** | 2 | **quant** | **42** |
| 3 | // | 1.0 | 1 | quant | 39 |
| 4 | // | 2.0 | 0.5 | 94 | 38 |
| 5 |  | 1.0 | 2 | 86 | 24 |
| 6 | $PhI(OAc)_2$ | 1.0 | 4 | quant | 16 |
| 7 | $H_2O_2$ | 5.0 | 0.5 | quant | 13 |
| 8 | $PhC(Me)_2OOH$ | 2.0 | 64 | 92 | 4 |
| 9 | NaOCl | 9.0 | 18 | quant | 16 |

[a] [CTAB]; 20 mol% ($6.55 \times 10^{-3}$ M)

**Table 2. Effect of Water Content in Asymmetric Oxidation of 1a to 2a**




| entry | toluene/$H_2O$ (v/v) | [$H_2O$]/[CTAB] | time (h) | yield | ee (%) |
|---|---|---|---|---|---|
| 1 | in toluene | 0 | 24 | trace | |
| 2 | 600 | 14 | 6 | quant | 26 |
| 3 | 120 | 70 | 2 | quant | 37 |
| 4 | **60** | **140** | **2** | quant | **42** |
| 5 | 30 | 280 | 4 | quant | 30 |
| 6 | 1 | | 12 | 87 | 17 |
| 7 | in $H_2O$ | | 18 | 85 | 12 |

[a] [CTAB]; $6.55 \times 10^{-3}$ M.

In reversed micelles, the water content that defines micelle size plays an important role both in reactivity and in enantioselectivity. The best optical yield (42% ee) of **2a** was obtained in toluene−$H_2O$ (60:1) (entry 4; Table 2), while the reaction yielded only a trace amount of **2a** in the absence of water. As water content exceeds the optimum amount, it becomes more difficult to form rigid reversed micelles and CTAB works merely as a phase-transfer catalyst. Therefore, in such cases (entries 5, 6; Table 2) both the reaction rate and the enantioselectivity decreased. Although CTAB can also form micelles in water, water micelles generally form structurally less rigid assemblies than that of reversed micelles. Thus, **2a** was obtained in 85% yield with only 12% ee (entry 7; Table 2).

Next, we optimized the chiral sources in the reaction. The best chemical and optical yields were obtained by the use of 10 mol % of di(2-MeO)benzoyl-L-tartaric acid (**3b**) (quant, 53% ee) (entry 9; Table 3). The use of other tartaric acid derivatives or chiral sources such as various carboxylic acids, a sulfonic acid, an N-protected amino acid, and a phosphonic acid did not improve the % ee of **2a**.

The present reaction is applicable to several sulfides (**1a**−**i**) and provides corresponding sulfoxides in nearly

(6) (a) Tascioglu, S. *Tetrahedron* **1996**, *52*, 11113−11152. (b) Zhang, Y.-M.; Sun, P.-P. *Tetrahedron: Asymmetry* **1996**, *7*, 3055−3058. (c) Zhang, Y.-M.; Wu, W. *Ibid.* **1997**, *8*, 2723−2725; 3575−3578. (d) Sun, P.-P.; Zhang, Y.-M. *Synth. Commun.* **1997**, *27*, 4173−4179.

(7) Zhang, Y.-M.; Fu, C.-L.; Fan, W.-Q. *Chin. J. Chem.* **1990**, *1*, 89−96 and references therein.

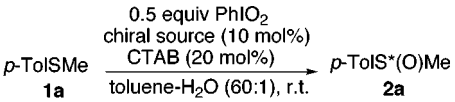
(8) Almost all highly enantioselective chemical oxidations of sulfides to sulfoxides reported so far have required more than stoichiometric amounts of chiral sources (or chiral oxidants) except for transition-metal-catalyzed reactions. Only chiral hydroperoxyflavin-mediated oxidation of sulfides achieved moderate enantioselectivities using a catalytic amount of chiral source: Shinkai, S.; Yamaguchi, T.; Manabe, O.; Toda, F. *J. Chem. Soc., Chem. Commun.* **1988**, 1399−1401. For a review, see: Kagan, H. B. Asymmetric Oxidation of Sulfides. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; pp 203−226 and references therein.

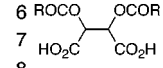
(9) (a) Formo, M. W.; Johnson, J. R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, pp 486−487. (b) Barton, D. H. R.; Godfrey, C. R. A.; Morzycki, J. W.; Motherwell, W. B.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1947−1952.

(10) The optical yield of the present reaction is remarkably affected by the choice of solvent. That is, better optical yields were observed with reversed micellar systems in nonpolar solvents (toluene: quant, 42% ee; *n*-hexane: quant, 37% ee; $CCl_4$: 97%, 34% ee) than with micelles in polar solvents ($CHCl_3$: quant, 0% ee; $CH_2Cl_2$: quant, 0% ee; MeCN: 88%, 1% ee; AcOEt: quant, 0% ee; acetone: trace) in the presence of **3a** (10 mol %), CTAB (20 mol %), and $H_2O$.

(11) No enhancement of ee of **2a** was observed when using various ratios and amounts of CTAB and **3a**. The ee of **2a** were 42% ee (CTAB/**3a** = 2; [**3a**] = 10 mol %), 35% ee (CTAB/**3a** = 1; [**3a**] = 10 mol %), 15% ee (CTAB/**3a** = 0.5; [**3a**] = 40 mol %), and 41% ee (CTAB/**3a** = 2; [**3a**] = 100 mol %).

**Table 3. Asymmetric Oxidation of 1a to 2a Using Various Chiral Sources**

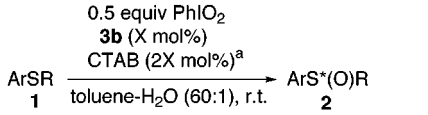



| entry | chiral source | yield (%) | ee (%) |
|---|---|---|---|
| 1 | (+)-10-camphorsulfonic acid | quant[a] | 0 |
| 2 | (*S*)-(+)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate | quant[a] | 3 [*R*] |
| 3 | *N*-phthaloyl-L-glutamic acid | 97 | 9 [*S*] |
| 4 | (*S*)-(+)-α-methoxyphenyl acetic acid | 76[a] | 31 [*R*] |
| 5 | (*R*)-(+)-1,1'-binaphthyl-2,2'-dicarboxylic acid | quant | 19 [*S*] |
| 6 |  R=Ph (D) **3a** | quant | 42 [*R*] |
| 7 | $^t$Bu (L) | 97 | 13 [*S*] |
| 8 | 2-Tol (L) | quant | 32 [*S*] |
| 9 | **2-MeOPh (L) 3b** | **quant** | **53** [*S*] |
| 10 | 2-Pr$^i$OPh (L) | quant | 24 [*S*] |
| 11 | 2,6-Me$_2$Ph (L) | 97 | 3 [*S*] |
| 12 | 2-naphthyl (L) | quant | 41 [*S*] |



a) 10 mol% of CTAB was used.

**Table 4. Catalytic Asymmetric Oxidation of 1 to 2**




| entry | substrate (**1**) Ar | R | | X | time (h) | yield (%)[b] | ee (%)[c,d] |
|---|---|---|---|---|---|---|---|
| 1 | 4-MePh | Me | **1a** | 10 | 2 | quant | 53 [*S*] |
| 2 | 4-NO$_2$Ph | Me | **1b** | 10 | 24 | 91 | 72 [*S*] |
| 3 | // | | | 1 | 72 | 24(95)[e] | 62 [*S*] |
| 4 | // | | | 50 | 5 | quant | 71 [*S*] |
| 5 | // | | | 100 | 3 | quant | 68 [*S*] |
| 6 | 3-NO$_2$Ph | Me | **1c** | 10 | 42 | 94 | 64 [*S*] |
| 7 | 4-NO$_2$Ph | Et | **1d** | 10 | 18 | 90 | 57 [*S*] |
| 8 | 4-CN | Me | **1e** | 10 | 12 | quant | 65 [*S*] |
| 9 | 4-Br | Me | **1f** | 10 | 12 | quant | 58 [*S*] |
| 10 | 4-MeO | Me | **1g** | 10 | 4 | quant | 46 [*S*] |
| 11 | 2-naphthyl | Me | **1h** | 10 | 48 | 90 | 51 [*S*] |
| 12 |  | | **1i** | 10 | 48 | 88 | 38 [*S*] |

[a][CTAB] = 6.55x10$^{-3}$ M [b]Yields refer to the average of at least two isolated yields. [c]Determined by HPLC analysis employing a Daicel Chiralcel OD, OJ, or Chiralpak AD, error ±2% of the stated value. [d]Absolute configurations were established by comparison of the sign of $[\alpha]_D$ to literature values. [e]Yield based on reacted substrate.

quantitative yields with moderate to good enantiomeric excesses when using **3b** as a chiral source (Table 4). As expected, similar optical yields were observed in the presence of either 1 mol %, 50 mol %, or 100 mol % of **3b**, although the reaction took longer to complete when small amounts of CTAB ($6.55 \times 10^{-3}$ M) were used (entries 2−5; Table 4).

Further kinetic study using methyl *p*-nitrophenyl sulfide (**1b**) as a model substrate yielded some information on the mechanism of this system. Sulfide **1b** was chosen because it has the best % ee and its moderate reaction rate allows easy detection of the change in % ee of **2b** as a function of reaction time. The results are shown in Figure 1.

The initial reaction rate with 1.0 equiv of PhI=O is approximately eight times faster than that with 0.5 equiv of $PhIO_2$ (Figure 1a,c). Interestingly, the % ee of **2b** increases during the course of the reaction when using 0.5 equiv of $PhIO_2$ (from 34% ee at 6% conversion to 72% ee at 95% conversion), while the % ee of **2b** stays nearly constant (38−48% ee) when using 1.0 equiv of PhI=O. In these cases, the kinetic resolution of **2b** cannot occur since the corresponding sulfone does not form at all.[12] Furthermore, the equivalency (either 0.5 equiv or 1.0 equiv) of $PhIO_2$ neither affected the yield nor the % ee of **2b** but did affect the reaction rate (Figure 1a,b). In addition, the oxidation of **1b** by $PhIO_2$ did not proceed at all without **3b**, while a 42% yield of **2b** was obtained after 70 min when using PhI=O even in the absence of **3b** (Figure 1d). The rate calculated from 10% consumption of reactant **1b** showed that the reaction rate without **3b** is ca. 15% of the rate observed with **3b**. Therefore, correcting for this background reaction from the reaction described in Figure 1d, the reaction pathway involving **3b** is expected to yield ca. 56% ee (Figure 1c,d). Thus, the higher enantioselectivity observed when using 0.5 equiv of $PhIO_2$ (72% ee) rather than 1.0 equiv of PhI=O (48% ee) seems to be partly caused by the unreactive nature of $PhIO_2$ in the absence of **3b**. These results suggest that there are other mechanistic reasons for the higher enantioselectivity when using 0.5 equiv of $PhIO_2$. Since the oxidant and **3b** might also be epimerizing the sulfoxide center, we examined the stability of an enantiomerically pure sulfoxide **2b** under the reaction conditions [the oxidant (1:1 PhI=O and $PhIO_2$), which seems to be generated in situ, 10 mol % **3b**, and 20 mol % CTAB in toluene−$H_2O$ (60:1)]. However, no change in the % ee was observed even after 2 days when using racemic sulfoxide **2b** as well as enantiomerically pure sulfoxide **2b**. This reaction does not seem to proceed via the simple mechanism of sequential reduction of PhI(V)$O_2$ to PhI(III)=O and then to PhI(I),[13] but via the in situ formation of some type of stereo-controlled reactive intermediate. Although we cannot clearly identify the reactive intermediate at this point, it may be an unprecedented reagent formed from $PhIO_2$, PhI=O, and the chiral tartaric acid **3b**.[14] As the reaction proceeds, the formed sulfoxide may perhaps be involved as well.

To summarize, the likely explanation of the successful catalytic asymmetric induction in our newly developed metal-free system is thought to be the following: (i) the in situ formation of stereocontrolled reactive species (the remarkable enhancement of the % ee of **2b** during the course of the reaction (Figure 1a,b)), (ii) the high coordination ability of the iodine(V) center similar to that of transition metal species (the best result (entry 9; Table 3) was derived from the putative coordination of the MeO group of **3b** to the iodine center; other noncoordinating oxidants gave only poor enantiomeric excesses), (iii)

(12) Several groups reported that a kinetic resolution of the formed sulfoxides to the corresponding sulfones enhances the % ee of the sulfoxides effectively in asymmetric oxidation reactions of sulfides; see: (a) Komatsu, N.; Hashizume, M.; Sugita, T.; Uemura, S. *J. Org. Chem.* **1993**, *58*, 7624−7626. (b) Yamanoi, Y.; Imamoto, T. *J. Org. Chem.* **1997**, *62*, 8560−8564. (c) Adam, W.; Korb, M. N.; Roschmann, K. J.; Saha-Möller, C. R. *J. Org. Chem.* **1998**, *63*, 3423−3428 (d) Palombi, L.; Bonadies, F.; Pazienza, A.; Scettri, A. *Tetrahedron: Asymmetry* **1998**, *9*, 1817−1822 and references therein.

(13) If the sequential reduction of $PhIO_2$ proceeds when using 0.5 equiv of $PhIO_2$, the initial ee value should be maximum and then decrease to the final ee. However, in this case, the enhancement of enantioselectivity occurs during the course of the reaction regardless of the equivalencies of $PhIO_2$.

(14) To confirm this, we examined the asymmetric oxidation of **1b** using the mixture of 0.1 equiv of PhI=O and 0.45 equiv of $PhIO_2$. As a result, no improvement of the final ee of **2b** (69% ee at 98% conversion) was observed, but the initial ee value increased (48% ee at 5% conversion).

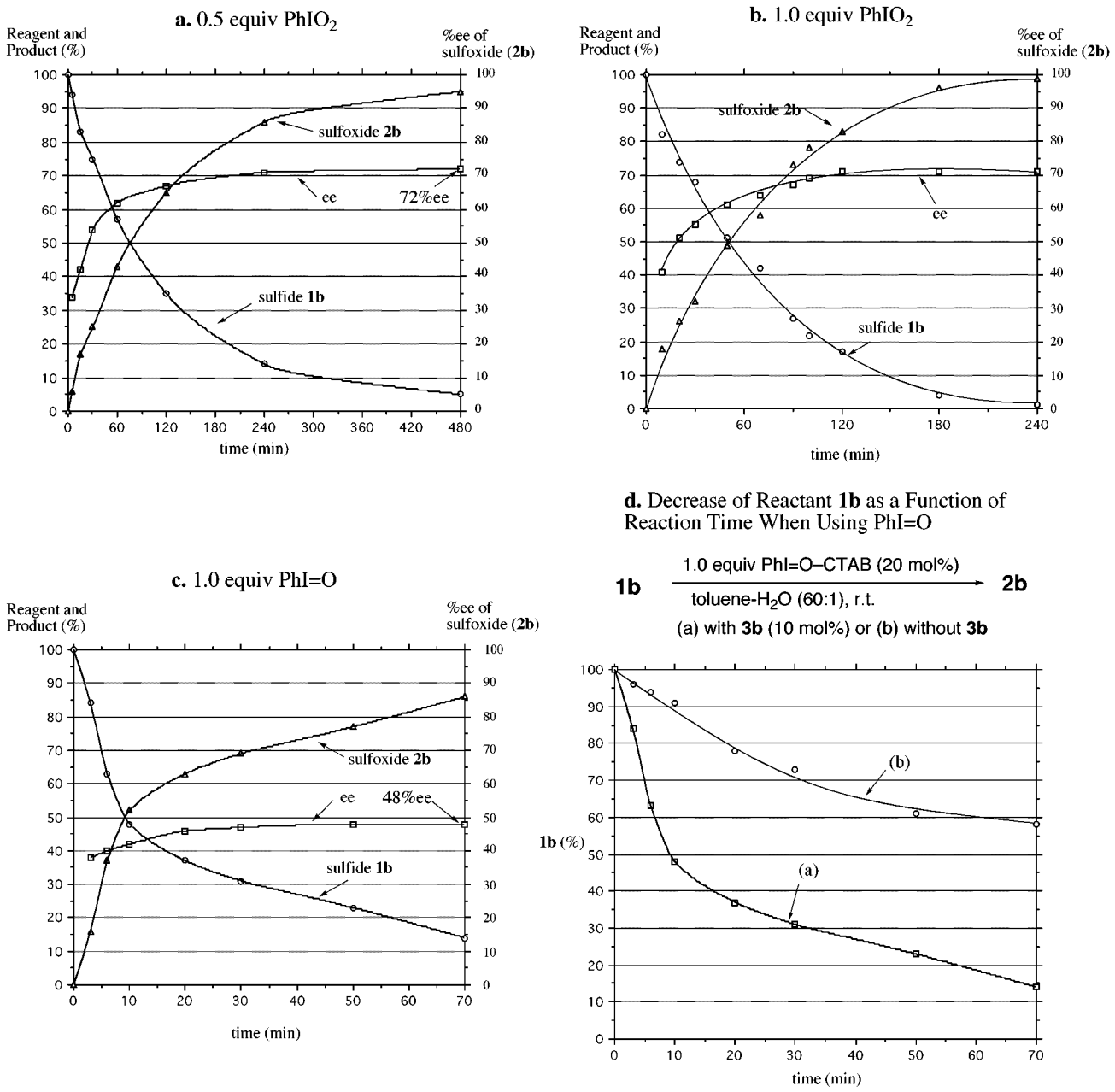



**Figure 1.** Asymmetric oxidation of sulfide **1b** as a function of reaction time (10 mol % **3b**; 20 mol % CTAB; toluene−$H_2O$ (60:1)) [yields and ee were determined by HPLC analysis of the crude reaction mixture on a chiral column (Daicel Chiralpak AD).]

reversed micellar effects which promote solubilization of $PhIO_2$ and provide well-defined reaction sites, and (iv) the extremely low reactivity of $PhIO_2$ in the absence of chiral activator **3b**. Although $PhIO_2$ has been used infrequently in organic synthesis[1] due to its insolubility in $H_2O$ and various organic solvents, we achieved the asymmetric oxidation of sulfides in greater efficiency than with PhI=O by exploiting exactly this property of $PhIO_2$, that is, its selective solubility.

## Conclusions

We accomplished an unprecedented catalytic asymmetric oxidation reaction of sulfides to sulfoxides using a still underexplored hypervalent iodine(V) reagent, $PhIO_2$, in high chemical yield with moderate to good enantiomeric excess in the presence of a catalytic amount of readily available **3b**. The application of this reversed micellar system to other stereoselective reactions and the clarification of the mechanism for the present asymmetric induction are now underway.

## Experimental Section

$^1H$ NMR (and $^{13}C$ NMR) spectra were recorded in $CDCl_3$, unless otherwise noted, with TMS or $CHCl_3$ as an internal standard. Infrared (IR) absorption spectra were recorded as a KBr pellet. Iodosobenzene was purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Iodoxybenzene was prepared according to literature procedure.[9] Sulfides (**1a**, **1b**, **1e**) were purchased from Aldrich. Sulfides (**1c**, **d**, **f**−**h**) were prepared from the corresponding thiophenols by alkylation with DBU and iodomethane or iodoethane.[15a] Sulfide **1i** was obtained by sodium reduction of benzothiophene.[15b] Yields refer to the average of at least two isolated yields. Yields of ≥99% were considered quantitative. All the enantiomeric excesses (ee) of

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**2a**−**i** were measured by chiral HPLC analysis: Daicel Chiralpak AD, Chiralcel OD, and Chiralcel OJ columns using a UV/vis detector or a multiwavelength detector.

**Di(2-methoxy)benzoyl-L-tartaric Acid (3b).** Chiral diacyltartaric acids were easily prepared in a manner similar to Yamamoto's method[16] in good yields.

**Preparation of 3b.** To a stirred suspension of dibenzyl-L-tartarate (200 mg, 0.606 mmol) and 2-methoxybenzoic acid (313 mg, 2.06 mmol) in benzene (4 mL) was added dropwise trifluoroacetic anhydride (0.324 mL, 2.24 mmol) over 10 min at room temperature and the mixture stirred for 1 h. To the reaction mixture was added aqueous saturated $NaHCO_3$ at 0 °C, and then the resulting mixture was extracted with $Et_2O$. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated. The residue was purified by column chromatography ($SiO_2$/*n*-hexane/$Et_2O$/$CH_2Cl_2$ = 6:1:5) to give dibenzyl-L-di(2-methoxy)benzoyltartarate **3′b** (362 mg, quant) as a colorless oil.

**3′b**: $^1$H NMR $\delta$ 3.81 (s, 6H), 5.14 (s, 4H), 6.00 (s, 2H), 6.85−6.93 (m, 4H), 7.12−7.22 (m, 10H), 7.45 (t, 2H, $J$ = 7.9 Hz), 7.78 (d, 2H, $J$ = 7.7 Hz); $^{13}$C NMR $\delta$ 55.8, 67.6, 71.1, 111.8, 117.7, 119.9, 128.0, 128.1, 128.2, 132.3, 134.2, 134.6, 159.8, 163.8, 165.5; IR (KBr) 1775, 1740, 1715, 1600 cm$^{-1}$; $[\alpha]^{25}_D$ = −13.1 (*c* 12.88, $CHCl_3$). Anal. Calcd for $C_{34}H_{30}O_{10}$: C, 68.22; H, 5.05. Found: C, 67.99; H, 5.21.

The solution of **3′b** (349 mg, 0.583 mmol) in AcOEt (13 mL) was hydrogenated by Pd-black (70.0 mg) under hydrogen atmosphere at 3 atm at room temperature. After 2 h, the mixture was filtered with Celite, and the filtrate was concentrated and recrystallized from $CHCl_3$ to give pure **3b** (243 mg, quant) as colorless needles.

**3b**: mp 187 °C dec (from $CHCl_3$); $^1$H NMR $\delta$ 3.36 (br, 2H), 3.80 (s, 6H), 5.92 (s, 2H), 6.87−6.90 (m, 4H), 7.42 (t, 2H, $J$ = 7.6 Hz), 7.89 (d, 2H, $J$ = 7.6 Hz); $^{13}$C NMR $\delta$ 55.9, 71.3, 112.0, 118.1, 120.1, 132.4, 134.3, 159.8, 164.2, 167.8; IR (KBr) 3235, 1775, 1740, 1715, 1600 cm$^{-1}$; $[\alpha]^{25}_D$ = −115.3 (*c* 7.13, acetone). Anal. Calcd for $C_{20}H_{18}O_{10}$: C, 57.42; H, 4.34. Found: C, 57.03; H, 4.45.

**General Procedure for Asymmetric Oxidation of Sulfides.** To a stirred suspension of CTAB (0.04 mmol) and **3b** (0.02 mmol) in toluene (5.0 mL) and $H_2O$ (0.10 mL) was added $PhIO_2$ (0.10 mmol), and the mixture was stirred for 1 h. Then, a solution of sulfide **1** (0.20 mmol) in toluene (1.0 mL) was added to the stirred suspension and was stirred for 2−48 h. The reaction mixture was quenched by the addition of aqueous saturated $NaHCO_3$ and then extracted with AcOEt, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography ($SiO_2$/$CH_2Cl_2$/acetone = 4:1) to give pure sulfoxide **2**, the enantiomeric excess of which was determined by HPLC. Absolute configurations were assigned by comparison of the sign of specific rotation with literature data.[17]

To confirm the reproducibility of the asymmetric oxidation of sulfides, these reactions were run at least twice. The conditions to determine the ee values and $[\alpha]_D$ values are as follows:

**(*S*)-Methyl *p*-tolyl sulfoxide (2a):** a colorless crystal; $^1$H NMR $\delta$ 2.42 (s, 3H), 2.71 (s, 3H), 7.33 (d, 2H, $J$ = 8.1 Hz), 7.54 (d, 2H, $J$ = 8.1 Hz); $^{13}$C NMR $\delta$ 21.4, 44.0, 123.4, 129.9, 141.3, 142.3. Daicel Chiralcel OD column at $\lambda$ = 243 nm, *n*-hexane/2-propanol (9:1) as eluent and a flow rate of 1.0 mL/min: $t_R$ (*R*) = 10.5 min, $t_R$ (*S*)= 11.3 min, ee = 53%; $[\alpha]^{25}_D$ −75.8 (*c* = 1.22, $CHCl_3$) (lit.[17c] ((*R*)-**2a**; 99.5% ee); $[\alpha]_D$ +145 (*c* = 0.75, $CHCl_3$)).

**(*S*)-Methyl 4-nitrophenyl sulfoxide (2b):** a colorless crystal; $^1$H NMR $\delta$ 2.77 (s, 3H), 7.84 (d, 2H, $J$ = 8.7 Hz), 8.40 (d, 2H, $J$ = 8.7 Hz); $^{13}$C NMR $\delta$ 43.8, 124.4, 124.6, 149.3, 153.1. Daicel Chiralpak AD column at $\lambda$ = 287 nm, *n*-hexane/2-propanol (94:6) as eluent and a flow rate of 1.0 mL/min: $t_R$ (*S*) = 48.7 min, $t_R$ (*R*) = 56.8 min, ee = 72%; $[\alpha]^{25}_D$ −112.4 (*c* = 1.32, $CHCl_3$) (lit.[17c] ((*R*)-**2b**; 99.3% ee); $[\alpha]_D$ +156.9 (*c* = 0.75, $CHCl_3$)).

**(*S*)-Methyl 3-nitrophenyl sulfoxide (2c):** a colorless crystal; $^1$H NMR $\delta$ 2.82 (s, 3H), 7.78 (t, 1H, $J$ = 7.9 Hz), 8.02 (d, 1H, $J$ = 7.7 Hz), 8.37 (d, 1H, $J$ = 7.7 Hz), 8.51 (s, 1H); $^{13}$C NMR $\delta$ 44.0, 118.9, 125.7, 129.2, 130.6, 148.6, 148.7.

Daicel Chiralcel OJ column at $\lambda$ = 243 nm, *n*-hexane/2-propanol (9:1) as eluent and a flow rate of 1.0 mL/min: $t_R$ (*R*) = 52.6 min, $t_R$ (*S*) = 59.3 min, ee = 64%; $[\alpha]^{25}_D$ −98.2 (*c* = 0.85, $CHCl_3$). Although the ee value of the literature[3d] was determined by $^1$H NMR using a chiral shift reagent, we determined the ee value of **2c** by HPLC analysis. (In our case, 71% ee was observed by NMR study as described in the literature.[3d])

**(*S*)-Ethyl 4-nitrophenyl sulfoxide (2d):** a colorless crystal; $^1$H NMR $\delta$ 1.17 (t, 3H, $J$ = 7.5 Hz), 2.69−2.76 (m, 1H), 2.93−2.99 (m, 1H), 7.73 (d, 2H, $J$ = 8.9 Hz), 8.32 (d, 2H, $J$ = 8.9 Hz); $^{13}$C NMR $\delta$ 5.6, 50.1, 124.2, 125.2, 149.4, 150.9. Daicel Chiralcel OD column at $\lambda$ = 291 nm, *n*-hexane/2-propanol (9:1) as eluent and a flow rate of 0.5 mL/min: $t_R$ (*R*) = 48.9 min, $t_R$ (*S*) = 52.0 min, ee = 57%; $[\alpha]^{25}_D$ −107.5 (*c* = 1.65, $CHCl_3$). The literature[17b] shows the enantiomeric resolution of racemic **2d** using a chiral column.

**(*S*)-4-Cyanophenyl methyl sulfoxide (2e):** a colorless crystal; $^1$H NMR $\delta$ 2.78 (s, 3H), 7.78 (d, 2H, $J$ = 8.5 Hz), 7.85 (d, 2H, $J$ = 8.5 Hz); $^{13}$C NMR $\delta$ 43.8, 114.6, 117.6, 124.2, 132.8, 151.3. Daicel Chiralcel OJ column at $\lambda$ = 267 nm, *n*-hexane/2-propanol (9:1) as eluent and a flow rate of 1.0 mL/min: $t_R$ (*R*) = 53.5 min, $t_R$ (*S*) = 59.6 min, ee = 65%; $[\alpha]^{25}_D$ −89.4 (*c* = 1.12, EtOH) (lit.[17d] ((*S*)-**2e**; 92% ee); $[\alpha]_D$ −120 (*c* = 1.07, EtOH)).

**(*S*)-4-Bromophenyl methyl sulfoxide (2f):** a colorless crystal; $^1$H NMR $\delta$ 2.72 (s, 3H), 7.52 (d, 2H, $J$ = 8.7 Hz), 7.67 (d, 2H, $J$ = 8.7 Hz); $^{13}$C NMR $\delta$ 43.9, 125.0, 125.3, 132.4, 144.7. Daicel Chiralcel OD column at $\lambda$ = 252 nm, *n*-hexane/2-propanol (99:1) as eluent and a flow rate of 0.8 mL/min: $t_R$ (*R*) = 85.1 min, $t_R$ (*S*) = 89.3 min, ee = 58%; $[\alpha]^{25}_D$ −75.7 (*c* = 1.50, $CHCl_3$) (lit.[3g] ((*S*)-**2f**; 79% ee); $[\alpha]_D$ −105.2 (*c* = 0.44, $CHCl_3$)).

**(*S*)-*p*-Anisyl methyl sulfoxide (2g):** a colorless oil; $^1$H NMR $\delta$ 2.70 (s, 3H), 3.86 (s, 3H), 7.03 (d, 2H, $J$ = 8.9 Hz), 7.60 (d, 2H, $J$ = 8.9 Hz); $^{13}$C NMR $\delta$ 43.9, 55.5, 114.8, 125.4, 136.5, 161.9. Daicel Chiralcel OD column at $\lambda$ = 243 nm, *n*-hexane/2-propanol (9:1) as eluent and a flow rate of 1.0 mL/min: $t_R$ (*R*) = 15.8 min, $t_R$ (*S*) = 17.3 min, ee = 46%; $[\alpha]^{25}_D$ −81.5 (*c* = 1.12, $CHCl_3$) (lit.[17c] ((*R*)-**2g**; 99.5% ee); $[\alpha]_D$ +165.9 (*c* = 0.38, $CHCl_3$)).

**(*S*)-Methyl 2-naphthyl sulfoxide (2h):** a colorless crystal; $^1$H NMR $\delta$ 2.73 (s, 3H), 7.51−7.54 (m, 3H), 7.85−7.93 (m, 3H), 8.15 (s, 1H); $^{13}$C NMR $\delta$ 43.7, 119.3, 123.9, 127.3, 127.7, 128.0, 128.4, 129.5, 132.8, 134.3, 142.6. Daicel Chiralpak AD column at $\lambda$ = 223 nm, *n*-hexane/2-propanol (95:5) as eluent and a flow rate of 0.5 mL/min: $t_R$ (*R*) = 64.5 min, $t_R$ (*S*) = 69.5 min, ee = 51%; $[\alpha]^{25}_D$ −69.9 (*c* = 1.38, acetone) (lit.[17c] ((*R*)-**2h**; 77.5% ee); $[\alpha]_D$ +102.6 (*c* = 1.9, acetone)).

**(*S*)-1-Thiaindane 1-oxide (2i):** a colorless oil; $^1$H NMR $\delta$ 3.23−3.41 (m, 3H), 3.82−3.90 (m, 1H), 7.40−7.54 (m, 3H), 7.84 (d, 1H, $J$ = 7.5 Hz); $^{13}$C NMR $\delta$ 31.4, 52.7, 126.0, 126.7, 128.2, 132.3, 143.1, 144.7. Daicel Chiralpak AD column at $\lambda$ = 267 nm, *n*-hexane/2-propanol (9:1) as eluent and a flow rate of 1.0 mL/min: $t_R$ (*S*) = 16.3 min, $t_R$ (*R*) = 19.3 min, ee = 38%; $[\alpha]^{25}_D$ +110.3 (*c* = 0.787, acetone) (lit.[17a] ((*R*)-**2i**; 2.6% ee); $[\alpha]_D$ −7.3 (*c* = 1.10, acetone), lit.[17e]((*R*)-**2i**; 99% ee); $[\alpha]_D$ −285 (*c* = 1.5, acetone)).

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