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Asymmetric oxidation of sulfides catalyzed by (*R*)-6,6'dibromo-BINOL derived titanium complex

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ABSTRACT

An efficient asymmetric oxidation of sulfides was achieved using (R)-6,6'-dibromo-BINOL as chiral ligand in combination with Ti(OⁱPr)₄ using 70% aqueous tertiary butyl hydroperoxide as oxidant. The resulting sulfoxides had high enantiopurities and good yields. A range of aryl alkyl and aryl benzyl sulfides were oxidized to the corresponding sulfoxides with 78–95% ee in 72–80% yields.

GRAPHICAL ABSTRACT



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KEYWORDS

(R)-6,6'-dibromo-BINOL; chiral sulfoxides; kinetic resolution; asymmetric oxidation

Introduction

Chiral sulfoxides are utilized as chiral auxiliaries in various asymmetric reactions.^[1] Some of them like esomeprazole, armodafinil, aprikalim, oxisurane and ustiloxine^[2] exhibit biological activities and thus find use as therapeutic agents. Generally, enantiopure sulfoxides are obtained either by nucleophilic displacement of diastereomeric sulfinates or resolution of racemic mixtures or by asymmetric oxidation of sulfides.^[3] Over the past two decades, the catalytic asymmetric oxidation of sulfides has been investigated extensively using transition metal complexes of various chiral ligands. Several catalyst systems for the asymmetric oxidation of sulfides have been reported including Ti(IV)-BINOL,^[4] C₂-symmetric diols,^[5] β -amino alcohols,^[6] and organic catalysts.^[7] Since the pioneering work on the asymmetric oxidation of sulfides involving the use of Ti(OⁱPr)₄/chiral tartrate systems reported by Kagan et al. and Modena et al. ^[8] the enantioselective oxidation of sulfides catalyzed by chiral complexes of transition metals such as titanium,^[9] vanadium,^[10] manganese,^[11] iron,^[12] with various types of chiral bidentate,^[13] tridentate,^[14] and tetradentate ligands have also been explored to catalyze asymmetric sulfoxidation of prochiral sulfides.

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Scheme 1. Synthesis of (R)-6,6'-dibromo-BINOL.

1,1'-Binaphthyl-2,2'-diol (BINOL) and its derivatives have generated particular interest because their versatile backbone can be modified, thereby affecting the reaction environment by influencing properties of the metal center. Uemura and coworkers reported the asymmetric oxidation of sulfides by using a Ti(IV) complex generated from Ti(O^{*i*}Pr)₄ and chiral binaphthol^[4]. Moderate yields and enantiomeric excesses were obtained at low temperatures; whereas high enantiomeric excesses and very low yields were reported at 25 °C. In these experiments CCl₄ was used as solvent. Enantiomers of 6,6'-dibromo-BINOL were effectively used as chiral ligands in various asymmetric reactions namely Mannich-Type reaction,^[15] Strecker-type reaction,^[16] Diels-alder reaction,^[17] carbonyl-ene cyclization,^[18] Friedel-crafts reaction.^[19] However, there have been no successful reports for the application of 6,6'-dibromo-BINOL as chiral ligand for the asymmetric oxidation of sulfides. Xian and coworkers reported^[20] a single reaction for the asymmetric oxidation of thioanisole using (S)-6,6'-dibromo-BINOL as chiral ligand. In this, lower enantioselectivities (enantiomeric excess is up to 43%) were observed when the reaction was performed at 0 °C. However, when the reaction was stirred for prolonged time at 25 °C, enantioselectivity was improved but chemical yield was very low (35%). This decrease in yield is attributed due to the formation of more sulfone. Here, decane solution of tertiary butyl hydroperoxide was used as oxidizing agent. In the presence of this oxidizing agent the rate of kinetic resolution is so fast that the formation of sulfone increases rapidly, and the yield decreases drastically with time. Therefore, finding suitable reaction conditions by using 6,6'-dibromo-BINOL as chiral ligand, which can minimize the sulfone formation and also afford good enantiomeric excess still remains an attractive goal. In this context, we wish to report efficient oxidation of sulfides to yield the sulfoxides with a high enantiomeric excess and good yields. By using 70% aq. tertiary butyl hydroperoxide instead of tertiary butyl hydroperoxide (in decane) as oxidizing agent we found that the oxidizing agent has a profound effect on the rate of kinetic resolution. With aq.solution of tertiary butyl hydroperoxide, kinetic resolution occurred in a controlled way, thus it controls the formation of sulfone.

Results and discussion

Synthesis of (R)-6,6'-dibromo-BINOL

(R)-6,6'-dibromo-BINOL was synthesized from the commercially available (R)-BINOL in single step by following the reaction (as shown in Scheme 1), reported in the literature.^[21]



Scheme 2. Asymmetric oxidation of methyl phenyl sulfide.

(*R*)-BINOL was reacted with Br_2 at -70° to -65° C in dichloromethane to get (*R*)-6,6'-dibromo-BINOL (*R*)-2.

In order to find the optimal conditions for asymmetric sulfoxidation using (R)-6,6'dibromo-BINOL as chiral ligand, methyl phenyl sulfide was chosen as a probe substrate (Scheme 2). Different metal complexes like Ti(OⁱPr)₄, VO(acac)₂, Cu(acac)₂, Fe (acac)₃ were explored in an attempt to find the suitable metal complex for this system. The oxidation of sulfide using VO(acac)₂, Cu(acac)₂ and Fe(acac)₃ afforded sulfoxide with very low enantiomeric excess (Table 1, entries 2–4). The use of Ti(OⁱPr)₄ afforded the sulfoxide with good enantiomeric excess (Table 1, entry 1 and 5). Hence, Ti(OⁱPr)₄ was selected as the suitable metal complex.

The effect of varied mole ratios of (R)-6,6'-dibromo-BINOL and Ti(OⁱPr)₄ on the asymmetric oxidation of methyl phenyl sulfide (Table 2) was studied. Mole ratios of (R)-6,6'-dibromo-BINOL were differed from 5 to 20 mole % and mole ratios of Ti(OⁱPr)₄ were differed from 2.5 to 10 mole %. It was observed that with an increase in mole ratios, there was no improvement in enantiomeric excess of sulfoxide. However, with the increase in mole ratios, sulfone formation was more and due to this sulfoxide was obtained with low yield. Based on the experimental results, 10 mole % of (R)-6,6'- dibromo-BINOL and 5 mole % of Ti(OⁱPr)₄ was selected as the optimum mole ratios for the reaction.

The impact of time and temperature on the outcome of oxidation was also studied. The reaction proceeds by two successive steps: initially sulfide is enantioselectively oxidized into sulfoxide and then oxidative kinetic resolution takes place. During kinetic resolution, predominantly, the less favored sulfoxide enantiomer gets over oxidized to form sulfone, which in turn enhances the enantiomeric excess of phenyl methyl sulfoxide.

When the reaction was carried out at 0 °C, sulfoxide was obtained with low enantiomeric excess and high yield (Table 3, entries 1 and 2). Reason for low enantiomeric excess is, at 0 °C the rate of kinetic resolution is slow and ineffective. When the reaction was carried out at 25 °C, sulfoxide was obtained with high enantiomeric excess and low yield (Table 3, entry 5). Reason for low yield is, at 25 °C kinetic resolution starts taking place even before the complete conversion of sulfide. Due to this, formation of sulfone is more. To get a compromise between enantiomeric excess and yield, initially the reaction was stirred at 0 °C till the maximum conversion of sulfide took place and then increased the temperature to 25 °C to allow the kinetic resolution to take place. With this telescopic method, sulfoxide was obtained with high enantiomeric excess and good yield (Table 3, entry 6).

The influence of different solvents on the oxidation of methyl phenyl sulfide (Table 4) was also explored. The oxidation of sulfide using either CH_2Cl_2 or hexane (Table 4, entries 3 and 4) afforded sulfoxide with low enantiomeric excess and low yield. The use of CCl_4 (Table 4, entry 2) afforded sulfoxide with good enantiomeric

		Metal complex						
Entry	Metal complex	(<i>R</i>)-2 (mol%)	(mol %)	Yield ^b (%)	ee ^c (%) (config.) ^d			
1	Ti(O ⁱ Pr) ₄	10	5	72	85 (<i>R</i>)			
2	Vo(acac) ₂	10	5	73	25 (<i>R</i>)			
3	Cu(acac) ₂	10	5	75	16 (<i>R</i>)			
4	Fe(acac) ₃	10	5	78	21 (<i>R</i>)			

Table 1. Asymmetric oxidation of methyl phenyl sulfide with different metal complexes under reaction conditions^a.

^aReaction conditions: Methyl phenyl sulfide (1 mmol), (R)-6,6'-dibromo-BINOL (10 mol%), metal complex, 70% aq. tertiary butyl hydroperoxide (2 equiv.), water (0.5 equiv.), toluene, at room temperature. Monitored the reaction using TLC until all the sulfide was consumed.

^bIsolated yield after column chromatography of the crude product.

^cDetermined by HPLC analysis on Chiralpak IC column.

^dAbsolute configuration was determined by the comparison of the sign of the specific rotation with that of reported in the literature.^{[9}a]

Table 2. Asymmetric oxidation of methyl phenyl sulfide with different mole ratios of (R)-2 and $Ti(O^{I}Pr)_{4}$ under reaction conditions^a.

	S CH	(<i>R</i>)- 2 , Ti(O ⁱ Pr 70% aq.TBHP (2 e) ₄ , equiv.)	S CH2	
		Toluene		Cin,	
Entry	(<i>R</i>)-2-Ti(O ⁱ Pr) ₄ (mol/mol)	(<i>R</i>)-2 (mol%)	Ti(O ⁱ Pr) ₄ (mol%)	Yield ^b (%)	ee ^c (%) (config.) ^d
1	1:0.5	20	10	68	87 (R)
2	1:0.5	15	7.5	74	85 (<i>R</i>)
3	1:0.5	10	5	80	95 (<i>R</i>)
4	1:0.5	5	2.5	81	82 (<i>R</i>)

^aReaction conditions: Methyl phenyl sulfide (1 mmol), (R)-6,6'-dibromo-BINOL, Ti(OⁱPr)₄, 70% aq. tertiary butyl hydroperoxide (2 equiv.), water (0.5 equiv.), toluene. Monitored the reaction using TLC until all the sulfide was consumed. ^bIsolated yield after column chromatography of the crude product.

^cDetermined by HPLC analysis on Chiralpak IC column.

^dAbsolute configuration was determined by the comparison of the sign of the specific rotation with that of reported in the literature.^[9a]

excess and good yield. The use of toluene as solvent afforded the sulfoxide with significance enhancement in enantioselectivity (Table 4, entry 1). Moreover, toluene as solvent offers significant safety benefits over CCl₄.

The impact of different oxidants on the oxidation of methyl phenyl sulfide was also examined (Table 5). Among these oxidants, with cumene hydroperoxide and 30% aq. H₂O₂ (Table 5, entries 2 and 3), sulfoxide was obtained with moderate yield and very low enantiomeric excess. With 70% aq. tertiary butyl hydroperoxide (Table 5, entry 1), sulfoxide was obtained with high enantiomeric excess and good yield. With tertiary butyl hydroperoxide (in decane), the reaction proceeded so quickly that within 3 h at 25 °C, yield of sulfoxide was decreased to as low as 30% (Table 5, entry 4) and after 14 h at 25 °C, no product could be isolated (Table 5, entry 5). It was observed that compared to tertiary butyl hydroperoxide (in decane), with 70% aq. tertiary butyl hydroperoxide the reaction proceeded in a controlled way so that the formation of sulfone is considerably reduced. Based on these results, 70% aq. tertiary butyl hydroperoxide was selected as the suitable oxidizing agent.

ig.)^d

81 (R)

92 (R)

95 (R)

CH ₃	$(R)-2 (10 \text{ mol }\%)$ $Ti(O^{i}Pr)_{4} (5 \text{ mol }\%)$ $70\% \text{ aq.TBHP (2 equiv.)}$ $Toluene$, С. С.Н.3
Temperature (°C)	Time	Yield ^b (%)	ee ^c (%) (conf
0	9 h	88	30 (<i>R</i>)
0	14 h	85	42 (<i>R</i>)
25	4 h	81	69 (R)

72

62

80

Table 3. Asymmetric oxidation of methyl phenyl sulfide with varied temperature and time under reaction conditions^a.

^aReaction conditions: Methyl phenyl sulfide (1 mmol), (R)-6,6'-dibromo-BINOL (10 mole%), Ti(OⁱPr)₄(5 mole%), 70% aq. tertiary butyl hydroperoxide (2 equiv.), water (0.5 equiv.), toluene. Monitored the reaction using TLC until all the sulfide was consumed.

9 h

14 h

5 h

9h

^bIsolated yield after column chromatography of the crude product.

25

25

0

25

^cDetermined by HPLC analysis on Chiralpak IC column.

Entry 1. 2. 3.

4.

5.

6.

^dAbsolute configuration was determined by the comparison of the sign of the specific rotation with that of reported in the literature.^[9a]

Table 4. Asymmetric oxidation of methyl phenyl sulfide catalyzed by (R)-2-Ti $(O'Pr)_4$ in different solvents^a.



Entry	Solvent	Yield ^b (%)	ee ^c (%) (config.) ^d
1.	Toluene	80	95 (<i>R</i>)
2.	CCl ₄	72	74 (<i>R</i>)
3.	CH ₂ Cl ₂	63	48 (<i>R</i>)
4.	Hexane	67	52 (<i>R</i>)

^aReaction conditions: Methyl phenyl sulfide (1 mmol), (*R*)-6,6'-dibromo-BINOL(10 mol%), Ti(OⁱPr)₄ (5 mol%), 70% aq. tertiary butyl hydroperoxide (2 equiv.), water (0.5 equiv.), solvent. Monitored the reaction using TLC until all the sulfide was consumed.

^bIsolated yield after column chromatography of the crude product.

^cDetermined by HPLC analysis on Chiralpak IC column.

^dAbsolute configuration was determined by the comparison of the sign of the specific rotation with that reported in the literature.^[9a]

In this invention, after charging $Ti(O^{i}Pr)_{4}$ and (R)-6,6'-dibromo-BINOL, 0.5 mole equiv. water is added to the catalytic system. Hypothesis on the effect of water is that the addition of water into $[Ti(O^{i}Pr)_{2}(BINOLato)]$ hydrolyzes a Ti-O-ⁱPr bond to form a μ -oxo bridge between two dimers (Ti-O-Ti), which acts as active catalyst for the asymmetric oxidation.

After establishing the optimum reaction conditions for asymmetric oxidation of phenyl methyl sulfide, these reaction conditions i.e., $5 \mod \% \operatorname{Ti}(O^{i}Pr)_{4}$, $10 \mod \%$ (*R*)-6,6'dibromo-BINOL, 0.5 mole. equiv. water, 2 mole equiv. 70% aq. tertiary butyl hydroperoxide, toluene as solvent, were then applied in the asymmetric oxidation of a number of aryl alkyl and aryl benzyl sulfides. The results are summarized in Table 6.



Table 5.	Asymmetric	oxidation	of	methyl	phenyl	sulfide	catalyzed	by	(<i>R</i>)-2-Ti(O ¹ Pr) ₄	using	differ-
ent oxida	nts. ^a										

Entry	Oxidant	Yield ^b (%)	ee ^c (%) (config.) ^d
1.	70% aq. TBHP (2 equiv.)	80	95 (R)
2.	CHP (2 equiv.)	60	20 (<i>R</i>)
3.	30% aq. H_2O_2 (2 equiv.)	65	32 (R)
4.	TBHP (in decane) (2 equiv.)	30	85 (<i>R</i>)
5.	TBHP (in decane) (2 equiv.)	0	-

^aReaction conditions: Methyl phenyl sulfide (1 mmol), (*R*)-6,6'-dibromo-BINOL(10 mol%), Ti(OⁱPr)₄ (5 mol%), Oxidant, water (0.5 equiv.), toluene. Monitored the reaction using TLC until all the sulfide was consumed.

^bIsolated yield after column chromatography of the crude product.

^cDetermined by HPLC analysis on Chiralpak IC column.

^dAbsolute configuration was determined by the comparison of the sign of the specific rotation with that reported in the literature.^[9a]

Table 6. Asymmetric oxidation of Sumdes with (R) -2-11(O Pr) ₄ under reaction co	conditions ⁻ .
--	---------------------------

S_D	(<i>R</i>)- 2 (10 mol %) Ti(O ⁱ Pr) ₄ (5 mol %)	S.NO
K K	70% aq.TBHP (2 equiv.) Toluene	R ^S R'

Entry	R	R′	Yield ^b (%)	ee ^c (%) (config.) ^d
1.	Phenyl	Methyl	80	95 (<i>R</i>)
2.	Phenyl	Ethyl	78	80 (R)
3.	<i>p</i> -Tolyl	Methyl	80	88 (R)
4.	4-Methoxy phenyl	Methyl	76	90 (R)
5.	4-Bromo phenyl	Methyl	72	82 (R)
6.	Phenyl	Benzyl	76	78 (<i>R</i>)

^aReaction conditions: Sulfide (1 mmol),(*R*)-6,6'-diphenyl-BINOL (10 mol%), Ti(OⁱPr)₄ (5 mol%), 70% aq. tertiary butyl hydroperoxide (2 equiv.), water (0.5 equiv.), toluene. Monitored the reaction using TLC until all sulfide was consumed.

^bIsolated yield after column chromatography of the crude reaction mixture.

^cFor entries 1–6, except for entry 3, chiral purity was determined by HPLC analysis on Chiralpak IC column, for entry 3 by using Chiralpak IA column.

^dAbsolute configuration was determined by the comparison of the sign of the specific rotation with that reported in the literature.^[9a,22]

As shown in Table 6, we have extended the applicability of the optimized reaction conditions to different alkyl aryl and aryl benzyl sulfides. Optically active sulfoxides were obtained with high enantiomeric excesses (up to 89%) with good chemical yields (up to 80%).

Conclusion

In summary, an efficient enantioselective sulfide oxidation is effected using (R)-6,6'dibromo-BINOL as chiral ligand. An important feature of this invention is control over the formation of over-oxidation product, sulfone. The presence of sulfone can make the isolation of pure sulfoxide tedious and it also impacts adversely on the overall yield of sulfoxide. With these improved reaction conditions, methyl phenyl sulfoxide can be prepared with high enantiomeric excess (up to 95%) and good yield (80%).

Experimental

General information

All the sulfides and all other reagents were procured from Sigma Aldrich and used directly without additional treatment. Commercial grade solvents were used for reaction and purification.¹H NMR (500 MHz) and ¹³C NMR (125 MHz) were obtained as solutions in deuterium substituted reagent on Bruker 500 MHz AVANCE III HD, Software-Topspin 3.5. Chemical shifts are reported in parts per million (ppm, δ). Melting points were recorded on Buchi M-560 melting point apparatus. Specific optical rotations were measured on Rudolph Research Analytical, Autopol V plus instrument. The ee values of the purified products were determined by HPLC on a chiral stationary phase using Chiralpak IA, Chiralpak IC columns with n-hexane/*i*-PrOH mixture as an eluent. Absolute configurations were assigned by comparison of the sign of the specific optical rotations with literature data.

General procedure for the catalytic oxidation of sulfides

To a solution of (*R*)-6,6'-dibromo-BINOL (0.72g, 1.62 mmol) in toluene (20 mL) were added Ti(OⁱPr)₄ (0.22 mL, 0.81 mmol), water (0.14 mL, 8 mmol) and stirred for 30 min at room temperature. To the resulting homogeneous solution was added methyl phenyl sulfide (2.0 g, 16.0 mmol), and the mixture was stirred at room temperature for 60 min. The solution was then cooled to 0–5 °C, 70% aqueous TBHP solution (4.4 mL, 32 mmol) was added slowly and stirred at 0–5 °C for 5 h. Increased the temperature to 25–30 °C and stirred for 9 h. The reaction mixture was concentrated under reduced pressure to obtain the crude product. This was further purified by column chromatography (ethyl acetate, cyclohexane 1:1) to get 1.80 g, (80% yield), of (*R*)-methyl phenyl sulfoxide (1a). $[\alpha]^{20}_{D} = +136$ (c = 1.7 in acetone); lit: $[\alpha]_{D} = +130$ (c = 1.7 in acetone) for (*R*), 89% $ee;^{[9}a]^{-1}$ H NMR (500 MHz, CDCl₃): δ 2.75 (s, 3H), 7.51–7.57 (m, 3H), 7.66–7.68 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 43.9, 123.5, 123.5, 129.3, 129.3, 131.0, 145.6; HPLC: t_R (*R*) = 24.1 min (major isomer), t_R (*S*) = 26.8 min (minor isomer) (Chiralpak IC column, n-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 240 nm).

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Supporting informations

Full experimental details, ¹H & ¹³C NMR spectra of the chiral ligand [(R)-2] and sulfoxides (1a-1f), HPLC traces of sulfoxides (1a-1f) can be found via the "Supplementary Content" section of this article's webpage.

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