

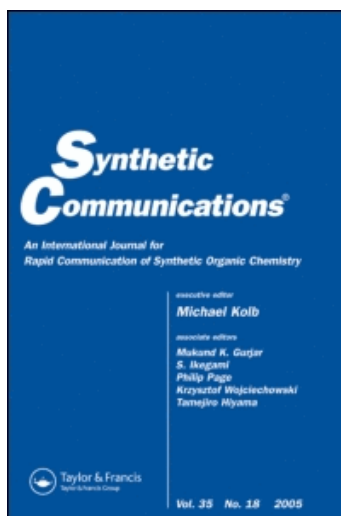
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### Efficient Synthesis of $\beta$ -Hydroxy Sulfides and $\beta$ -Hydroxy Sulfoxides Catalyzed by Cu/MgO Under Solvent-Free Conditions

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## EFFICIENT SYNTHESIS OF $\beta$ -HYDROXY SULFIDES AND $\beta$ -HYDROXY SULFOXIDES CATALYZED BY Cu/MgO UNDER SOLVENT-FREE CONDITIONS

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Maddeboina Krishnaiah, Boyapati Veeranjanyulu,  
and Dega Sudhakar**

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*Regio-, stereo-, and chemoselective ring opening of epoxides with thiols using Cu/MgO as a heterogeneous catalyst has efficiently been carried out to produce the corresponding  $\beta$ -hydroxy sulfides in excellent yields at room temperature under solvent-free conditions. The treatment of the epoxides with thiols and 50% aqueous  $H_2O_2$  in the presence of the same catalyst at room temperature affords the  $\beta$ -hydroxy sulfoxides in excellent yields.*

**Keywords:** Cu/MgO; epoxide;  $H_2O_2$ ;  $\beta$ -hydroxy sulfide;  $\beta$ -hydroxy sulfoxide; thiol

### INTRODUCTION

$\beta$ -Hydroxy sulfides are important intermediates for the synthesis of pharmaceuticals and natural products.<sup>[1–3]</sup> The ring opening of epoxides with thiols is a straightforward route to  $\beta$ -hydroxy sulfides. The conversion usually takes place in the presence of a promoter such as alumina,<sup>[4]</sup> silica gel,<sup>[5]</sup> resin,<sup>[6]</sup> or a common/complex Lewis acid.<sup>[7–13]</sup> However, harsh reaction conditions, long reaction times, poor yields, and use of an expensive catalyst are drawbacks in many of the methods. Here we report an efficient method for the preparation of  $\beta$ -hydroxy sulfides by ring opening of epoxides with thiols in the presence of Cu/MgO as a heterogeneous catalyst. The method has also been extended for the preparation of  $\beta$ -hydroxy sulfoxides using the same catalyst.

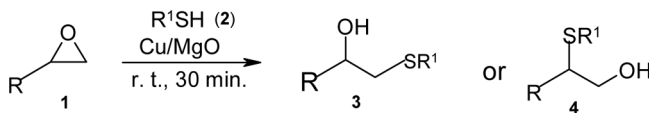
### RESULTS AND DISCUSSION

In continuation of our work<sup>[14–16]</sup> on the development of useful synthetic methodologies, we have observed that the ring opening of epoxides with thiols can be carried out efficiently using Cu/MgO as a catalyst at room temperature (Scheme 1).

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**Scheme 1.** Synthesis of  $\beta$ -hydroxy sulfides from epoxides using Cu/MgO.

A series of epoxides was converted into the corresponding  $\beta$ -hydroxy sulfides on treatment with different thiols following this procedure (Table 1). The conversion was complete within 20–30 min. The products were formed in excellent yields (82–95%). 2-Phenyl, 2-alkyl, and bicyclic epoxides underwent the conversion smoothly. Both aromatic and aliphatic thiols afforded the products with equal ease.

The formation of  $\beta$ -hydroxy sulfides from epoxides took place with high regio-, stereo-, and chemoselectivity. 2-Phenyl epoxide formed the products by attack of the thiols mainly at the benzylic position, and 2-alkyl epoxides furnished the products by attack at the terminal position. The  $^1\text{H}$  NMR spectra of the crude products showed the formation of only **3** from 2-alkyl epoxides and the formation of **4** (along with a minor amount of **3**) from styrene oxide.

The ring opening of a bicyclic epoxide with a thiol occurred with *anti* selectivity to form the product with *trans* configuration. In the  $^1\text{H}$  NMR spectrum of the product, the coupling constants of the ring protons adjacent to the  $-\text{OH}$  and  $-\text{SR}^1$  groups support this stereochemical assignment. For example, the  $J$  values of these two protons for **3n** (Table 1) are 9.5, 9.0, and 4.2 Hz and 9.2, 9.0, and 4.0 Hz, suggesting the *trans* configuration of the compound.

The present conversion is also chemoselective, because an epoxide opened with a thiol containing a hydroxyl group afforded only the sulfide (not a thiol) (Table 1, entries d, e, and r), indicating that the hydroxyl group did not attack the epoxide ring.

The work has been extended to the one-pot preparation of  $\beta$ -hydroxy sulfoxides, which are also important intermediates in organic synthesis for the preparation of natural products.<sup>[17–19]</sup> There are only a limited number of methods for one-pot conversion of epoxides into  $\beta$ -hydroxy sulfoxides.<sup>[20,13]</sup> These compounds can be prepared by treatment of epoxides with thiols and 50% aqueous  $\text{H}_2\text{O}_2$  in the presence of the same catalyst (Cu/MgO) at room temperature (Scheme 2).

Various epoxides were reacted with different thiols following this method to form a series of  $\beta$ -hydroxy sulfoxides (Table 2). The conversion was complete within 70 min in water medium, and the products were formed in excellent yields. All alkyl epoxides afforded only one regioisomer formed by attack of the thiols at the terminal position followed by oxidation. The bicyclic cyclohexene oxide furnished the *trans* product (Table 2, entry j). Two diastereomers (82:18) of this product was separated by column chromatography. However, the diastereomers of the other products could not be separated. Both aromatic and aliphatic thiols were applied for the preparation of  $\beta$ -hydroxy sulfoxides. Here also a thiol containing a hydroxyl group afforded only a  $\beta$ -hydroxy sulfoxide. No sulfone could be detected.

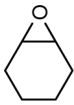
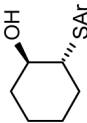
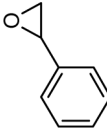
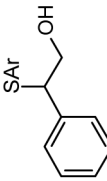
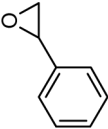
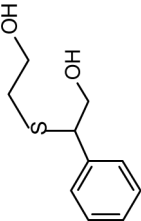
The catalyst, Cu/MgO,<sup>[21,22]</sup> works under heterogeneous conditions. It can conveniently be handled and removed from the reaction mixture. It is inexpensive and can easily be prepared from the readily available  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$  following the coprecipitation method. The catalytic activity of Cu/MgO in organic

**Table 1.** Thiolysis of epoxides catalyzed by Cu/MgO<sup>a</sup>

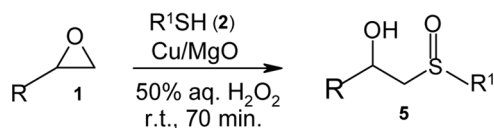
Entry	Epoxide (1)	Thiol (2)	Product (3/4)	Time (min)	Isolated yield (%) <sup>b</sup>
a		<p>C<sub>6</sub>H<sub>5</sub>SH <i>p</i>-Me-C<sub>6</sub>H<sub>4</sub>SH <i>p</i>-Cl-C<sub>6</sub>H<sub>4</sub>SH</p>		20	94
b					91
c					92
d		<p>HS-CH<sub>2</sub>-CH<sub>2</sub>-OH</p>		30	85
e					
f		<p>C<sub>6</sub>H<sub>5</sub>SH <i>p</i>-Me-C<sub>6</sub>H<sub>4</sub>SH <i>p</i>-Cl-C<sub>6</sub>H<sub>4</sub>SH</p>		30	94
g					95
h					92
i		<p>C<sub>6</sub>H<sub>5</sub>SH <i>p</i>-Me-C<sub>6</sub>H<sub>4</sub>SH <i>p</i>-Cl-C<sub>6</sub>H<sub>4</sub>SH</p>		30	90
j					88
k					89

(Continued)

Table 1. Continued

Entry	Epoxide (1)	Thiol (2)	Product (3/4)	Time (min)	Isolated yield (%) <sup>b</sup>
l		$\text{C}_6\text{H}_5\text{SH}$ $p\text{-Me-C}_6\text{H}_4\text{SH}$ $p\text{-Cl-C}_6\text{H}_4\text{SH}$	 <b>3l</b> Ar = $\text{C}_6\text{H}_5$ <b>3m</b> Ar = $\text{C}_6\text{H}_4\text{-}p\text{-Me}$ <b>3n</b> Ar = $\text{C}_6\text{H}_4\text{-}p\text{-Cl}$	20	90
m					92
n					88
o		$\text{C}_6\text{H}_5\text{SH}$ $p\text{-Me-C}_6\text{H}_4\text{SH}$ $p\text{-Cl-C}_6\text{H}_4\text{SH}$	 <b>4a</b> Ar = $\text{C}_6\text{H}_5$ <b>4b</b> Ar = $\text{C}_6\text{H}_4\text{-}p\text{-Me}$ <b>4c</b> Ar = $\text{C}_6\text{H}_4\text{-}p\text{-Cl}$	15	76 (12)
p					78 (10)
q					75 (15)
r		$\text{HS-CH}_2\text{-CH}_2\text{-OH}$	 <b>4d</b>	30	68 (18)

<sup>a</sup>The structures of the products were established from their spectral (<sup>1</sup>H NMR and MS) data.<sup>b</sup>Yields reported in the parentheses are for other regioisomers.



**Scheme 2.** Synthesis of  $\beta$ -hydroxy sulfoxides from epoxides using Cu/MgO.

synthesis has not yet been properly explored. Here this catalyst has been found to be highly effective for the preparation of  $\beta$ -hydroxy sulfides and  $\beta$ -hydroxy sulfoxides. In absence of this catalyst, the present conversion afforded the products with poor yields after longer reaction time.

## CONCLUSION

In conclusion, we have developed efficient, mild, and selective methods for organic solvent-free, high-yielding synthesis of  $\beta$ -hydroxy sulfides and  $\beta$ -hydroxy sulfoxides using very small quantities of an ecofriendly heterogeneous catalyst, Cu/MgO, for the first time.

## EXPERIMENTAL

### General Procedure for the Synthesis of $\beta$ -Hydroxy Sulfides

Cu/MgO (5 mg) was added to a mixture of an epoxide (2 mmol) and a thiophenol (2 mmol). The mixture was stirred at room temperature, and the reaction was monitored by thin-layer chromatography (TLC). After completion, the reaction mixture was diluted with EtOAc (10 mL) and filtered to remove the catalyst. The filtrate was concentrated, and the residue was subjected to column chromatography (silica gel, hexane–EtOAc) to obtain pure  $\beta$ -hydroxy sulfide.

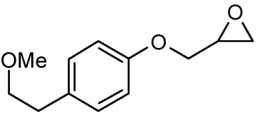
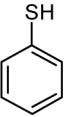
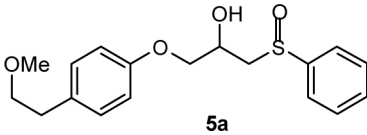
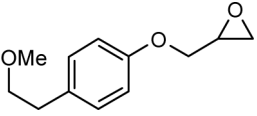
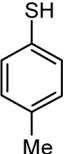
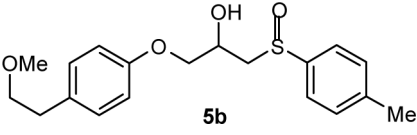
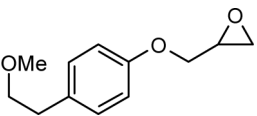
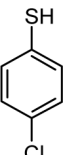
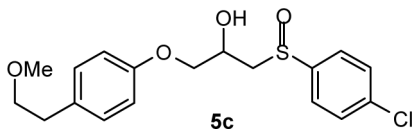
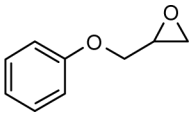
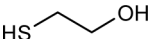
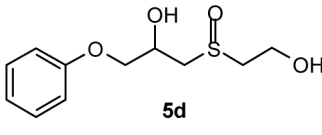

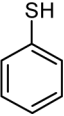
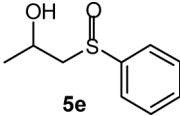

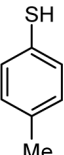
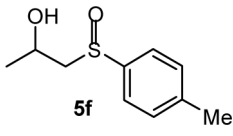
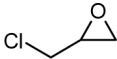
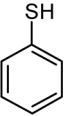
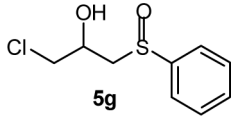
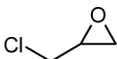
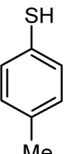
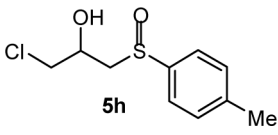
### General Procedure for the Synthesis of $\beta$ -Hydroxy Sulfoxides

Cu/MgO (5 mg) was added to a mixture of an epoxide (2 mmol) and a thiophenol (2 mmol). The mixture was stirred at room temperature. After completion of the ring-opening reaction (monitored by TLC), 50% aqueous  $\text{H}_2\text{O}_2$  (4 mL) was added at  $0^\circ\text{C}$  over 5 min. The reaction mixture was stirred continuously at room temperature. At the end of the reaction, excess  $\text{H}_2\text{O}_2$  was destroyed by addition of saturated aqueous  $\text{Na}_2\text{SO}_3$  solution. The mixture was extracted with EtOAc ( $3 \times 10$  mL), and the total extract was dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by column chromatography (silica gel, hexane–EtOAc) to isolate pure  $\beta$ -hydroxy sulfoxide.

### Spectral Data for Unknown Compounds

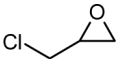
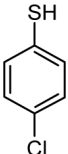
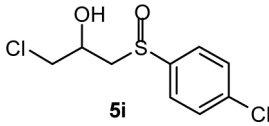
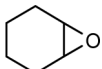
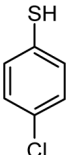
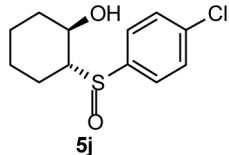
The spectral ( $^1\text{H}$  NMR and MS) and analytical data of the unknown products are given below.

**Table 2.** Synthesis of  $\beta$ -hydroxy sulfoxides catalyzed by Cu/MgO<sup>a</sup>

Entry	Epoxide	Thiol	Product (5)	Isolated yield (%)
a			 <b>5a</b>	91
b			 <b>5b</b>	89
c			 <b>5c</b>	90
d			 <b>5d</b>	85
e			 <b>5e</b>	87
f			 <b>5f</b>	85
g			 <b>5g</b>	91
h			 <b>5h</b>	89

(Continued)

Table 2. Continued

Entry	Epoxide	Thiol	Product (5)	Isolated yield (%)
i			 <b>5i</b>	91
j			 <b>5j</b>	82 <sup>b</sup>

<sup>a</sup>The structures of the products were established from their spectral (<sup>1</sup>H NMR and MS) data.

<sup>b</sup>Diastereomeric (82:18) mixture determined by <sup>1</sup>H NMR analysis.

**Compound 3d.** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  7.09 (2H, d,  $J$  = 8.0 Hz), 6.80 (2H, d,  $J$  = 8.0 Hz), 4.10 (1H, m), 3.99–3.92 (2H, m), 3.84 (1H, m), 3.72 (1H, m), 3.56–3.49 (2H, m), 3.34 (3H, s), 2.89–2.70 (6H, m); ESIMS:  $m/z$  309 [M + Na]<sup>+</sup>.

**Compound 3g.** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  7.30 (2H, d,  $J$  = 8.0 Hz), 7.09 (2H, d,  $J$  = 8.0 Hz), 3.82 (1H, m), 3.64 (2H, d,  $J$  = 4.0 Hz), 3.15–2.93 (2H, m), 2.66 (1H, brs), 2.32 (3H, s); ESIMS:  $m/z$  241, 239 [M + Na]<sup>+</sup>.

**Compound 3n.** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  7.39 (2H, d,  $J$  = 8.0 Hz), 7.27 (2H, d,  $J$  = 8.0 Hz), 3.28 (1H, ddd,  $J$  = 9.5, 9.0, 4.2 Hz), 2.78 (1H, brs), 2.70 (1H, ddd,  $J$  = 9.2, 9.0, 4.0 Hz), 2.20–2.01 (2H, m), 1.80–1.61 (2H, m), 1.38–1.16 (4H, m); ESIMS:  $m/z$  267, 265 [M + Na]<sup>+</sup>.

**Compound 4b.** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  7.31–7.14 (7H, m), 7.01 (2H, d,  $J$  = 8.0 Hz), 4.19 (1H, t,  $J$  = 7.0 Hz), 3.82 (2H, d,  $J$  = 7.0 Hz), 2.31 (3H, s); ESIMS:  $m/z$  267 [M + Na]<sup>+</sup>.

**Compound 5d.** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  7.32–7.15 (2H, m), 6.97–6.83 (3H, m), 5.77 (1H, brs), 5.30 (1H, brs), 4.48 (1H, m), 4.05–3.87 (4H, m), 3.57–3.40 (2H, m), 3.31–3.11 (2H, m); ESIMS:  $m/z$  267 [M + Na]<sup>+</sup>.

**Compound 5f.** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (2H, d,  $J$  = 8.0 Hz), 7.39 (2H, d,  $J$  = 8.0 Hz), 4.26 (1H, m), 3.42 (1H, brs), 3.21–3.01 (2H, m), 2.49 (3H, s), 1.22 (3H, d,  $J$  = 7.0 Hz); ESIMS:  $m/z$  221 [M + Na]<sup>+</sup>.

**Compound 5j (major diastereomer).** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  7.68 (2H, d,  $J$  = 8.0 Hz), 7.52 (2H, d,  $J$  = 8.0 Hz), 4.69 (1H, brs), 4.02 (1H, ddd,  $J$  = 9.5, 9.0, 4.2 Hz), 2.62 (1H, ddd,  $J$  = 9.5, 9.0, 4.5 Hz), 2.20–2.01 (2H, m), 1.81–1.60 (2H, m), 1.50–1.09 (4H, m); ESIMS:  $m/z$  283, 281 [M + Na]<sup>+</sup>.



**Compound 5j (minor diastereomer).**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58–7.47 (4H, brs), 3.85 (1H, ddd,  $J=9.5, 9.0, 4.0$  Hz), 3.31 (1H, brs), 2.51 (1H, ddd,  $J=9.2, 9.0, 4.0$  Hz), 2.17–1.91 (2H, m), 1.89–1.62 (2H, m), 1.49–1.10 (4H, m); ESIMS:  $m/z$  283, 281  $[\text{M} + \text{Na}]^+$ .

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