## A General and Efficient Method for the Selective Synthesis of β-Hydroxy Sulfides and β-Hydroxy Sulfoxides Catalyzed by Gallium(III) Triflate

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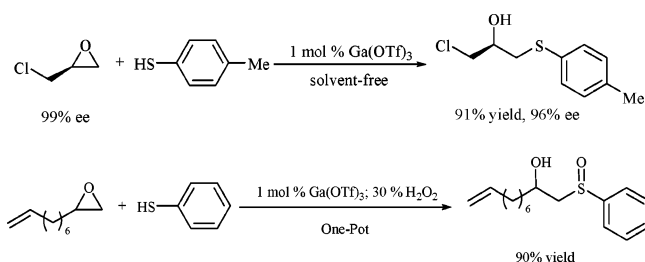
Gallium(III) triflate-catalyzed ring opening of epoxides affords β-hydroxy sulfides with high regioselectivity and chemoselectivity in high yields (84−97%) under solvent-free conditions. Additionally, a simple, efficient, and environmentally benign one-pot procedure for the synthesis of β-hydroxy sulfoxides in sole water has been developed for the first time. The process, promoted by a H_2O_2−Ga(OTf)$_3$ system, affords β-hydroxy sulfoxides in high yields (81−94%) and high chemoselectivity without any detectable overoxidation to β-hydroxy sulfones. The catalyst could be recovered easily after the reactions and reused without evident loss of activity.

Epoxides are often used as intermediates in organic synthesis,[1] and their reactions with different nucleophiles (e.g., amines, thiols, alcohols, etc.) have been the subject of extensive studies.[2] Thiolysis reaction of epoxides is the most practically and widely used route for the synthesis of β-hydroxy sulfides. It can be catalyzed by Lewis acid,[3] microwave irradiation,[4] or PBu$_3$.[5] Recently, we have studied the thiolysis reaction of epoxides in ionic liquids without any catalyst.[13d] β-Hydroxy sulfides[6] and β-hydroxy sulfoxides[7] are important intermediates in organic synthesis.

The oxidation of β-hydroxy sulfides is the most straightforward method for the synthesis of β-hydroxy sulfoxides. The selective oxidation of sulfides to sulfoxides has been a challenge for many years. Much effort has been devoted to develop a large number of oxidants to convert sulfides into sulfoxides.[8] Aqueous hydrogen peroxide is an ideal oxidant[9] in view of an effective oxygen content of as high as 47%, and water is the only theoretical byproduct. These obvious advantages have spurred the development of useful procedures for H_2O_2 oxidation of sulfides.[10]

Although a variety of catalytic systems have been introduced for oxidation of sulfides, however, many of these methodologies are associated with one or more disadvantages such as relatively long reaction time, environmentally unfriendly catalyst, low yield, the use of volatile organic solvents, requirement of excess reagents or catalysts, and harsh reaction conditions. For the synthesis of β-hydroxy sulfoxides, very little attention was paid to it.[6,11] Due to the importance of these compounds in organic synthesis, the development of environmentally benign, high-yielding, and clean approaches for the synthesis of β-hydroxy sulfides and β-hydroxy sulfoxides is in demand.

Metal triflates have advantages of water-tolerance, air-stability, recoverability of the agent from water, operational

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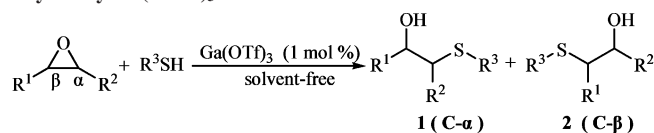(9) Sato, K.; Aoki, M.; Noyori, R. *Science* **1998**, *281*, 1646.

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TABLE 1. Thiolysis of Epoxides Catalyzed by Ga(OLTf)₃ under Solvent-Free Conditions[a]

entry	product	time (h)	yield (%)[b]	α/β[c]	entry	product	time (h)	yield (%)[b]	α/β[c]
1	**1a**	0.5	95	>98/2	11	**1k**	2	79(87)	>98/2
2	**1b**	0.5	89	>98/2	12	**1l**	0.5	95	>98/2
3	**1c**	0.6	91	>98/2	13	**1m**	0.6	84	>97/3
4	**1d**	0.5	91	>97/3	14	**1n**	1	60(89)[e]	>98/2
5	**1e**	0.6	97	>99/1	15	**1o**	0.5	91	>98/2 (96% ee)[f]
6	**1f** **2f**	0.7	86 (47)[d]	>3/97 (>40/60)[d]	16	**1p**	0.5	90	>98/2 (94% ee)[f]
7	**1g** **2g**	0.5	84 (41)[d]	>2/98 (>45/55)[d]	17	**1q**	0.5	89	>96/4
8	**1h**	0.5	89	-	18	**1r**	0.6	92	>99/1
9	**1i**	0.5	88	-	19	**1s**	0.6	85	-
10	**1j**	1.5	65(86)[e]	-	20	**1t**	0.5	89	>99/1
					21	**1u**	0.6	90	>99/1
					22	**1v**	0.5	91	>99/1

[a] Reaction conditions: epoxides (5 mmol), thiophenols (5 mmol), Ga(OTf)₃ (1 mol %), 30 °C. [b] Isolated yield. [c] Ratios of the two regioisomers were determined by ¹H NMR. [d] In the absence of Ga(OTf)₃. [e] CH₃NO₂ was used as solvent. [f] Determined by HPLC apparatus fitted with a Chiralcel OJ-H chiral column (*i*PrOH/hexane = 1/99; flow rate = 0.8 mL/min; detector = 254 nm).
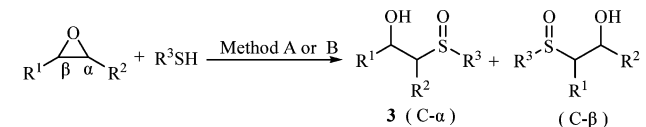
simplicity, strong tolerance to oxygen, nitrogen, phosphorus, and sulfur-containing reaction substrates and functional groups.[12] Recently, we have successfully applied metal triflates into several reactions.[13] In continuation of our interest in green chemistry and Lewis acid-catalyzed organic reactions,[13] we

herein developed a green, simple, and practical method for the synthesis of β-hydroxy sulfides and β-hydroxy sulfoxides from epoxides and thiophenols using Ga(OTf)₃ as catalyst under solvent-free or sole water conditions.

Initially, we have investigated a variety of ring-opening reaction conditions with the model reaction.[14a] It seems that nitromethane is a much better solvent (yield 84%) than all others

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TABLE 2. One-pot Synthesis of β-Hydroxy Sulfides Catalyzed by H$_2$O$_2$−Ga(OTf)$_3$[a]

entry	product	method	time (min)	yield (%)[b]	α/β[d]	dr[e]
1	3a	A	30	88	-	83:17
		B	60	90 (89)[c]		
2	3b	A	30	91	-	68:32
		B	60	90		
3	3c	A	53	83	-	85:15
		B	70	87 (88)[c]		
4	3d	A	35	89	>99/1	[f]
		B	60	91		
5	3e	A	35	93	>99/1	47:53
		B	60	94		
6	3f	A	40	87	>99/1	40:60
		B	60	88		
7	3g	A	35	89	>99/1	44:56
		B	60	89		
8	3h	A	56	82	>98/2	40:60
		B	70	87		
9	3i	A	50	86	97/3	[f]
		B	70	90		
10	3j	A	55	81	96/4	[f]
		B	70	84		
11	3k	A	45	87	95/5	61:39
		B	80	90		
12	3l	A	35	86	>98/2	45:55
		B	60	89		
13	3m	A	40	85	>99/1	38:62
		B	75	90		

[a] Reaction conditions: epoxides (5 mmol), thiophenols or thiols (5 mmol), Ga(OTf)$_3$ (1 mol %), and 30% H$_2$O$_2$ (10 mmol), 30 °C. Method A: Ga(OTf)$_3$ and H$_2$O$_2$ were added simultaneously. Method B: Ga(OTf)$_3$ was added and stirred for 30 min without solvent, followed by addition of H$_2$O$_2$. [b] Isolated total yield. [c] Oxidation of pure β-hydroxy sulfide **1h** at 30 °C for 25 min. [d] Determined by ^{1}H NMR analysis or HPLC. [e] Determined by HPLC apparatus fitted with a C$_{18}$ column (CH$_3$OH/H$_2$O = 35/65, flow rate = 1.0 mL/min; detector = 206 nm). [f] Not determined.

tested [water (70%), acetonitrile (73%), nitroethane (79%), and dichloromethane (67%)]. The best results were obtained by carrying out the reaction at 30 °C for 30 min using 1 mol % of Ga(OTf)$_3$ without solvent. The product **1a** was obtained in good to excellent yields, while **1a** was obtained in only low yield in the absence of metal triflates. Metal triflates examined showed good catalytic effects, and unexpectedly, Ga(OTf)$_3$ was particularly effective for this ring-opening reaction. In this reaction, Ga(OTf)$_3$ could be reused three times without any loss of activity. In contrast, other Lewis acids, such as InCl$_3$,[5d] produce a lower yield (53%) at the first use.

In light of this, subsequent studies were carried out under the optimized conditions: with 1 mol % of Ga(OTf)$_3$ at 30 °C under solvent-free. In all cases, Ga(OTf)$_3$-catalyzed reactions proceeded smoothly and gave the corresponding products in good to excellent yield, as shown in Table 1.

The selective nucleophilic attack of thiophenols occurred almost exclusively on the less hindered α-carbon of the oxirane ring. Interestingly, thiolysis reaction of styrene oxide afforded the β-addition products predominantly by attacking at the benzylic β-carbon with electronic effects. However, when the same reaction was performed in the absence of Ga(OTf)$_3$, the regioselectivity and conversions of ring-opening reactions were unsatisfactory (entries 6 and 7).

On the other hand, it was observed that thiophenols bearing either electron-donating or electron-withdrawing groups did not make any difference in this reaction. The chemoselective thiolysis in the presence of unprotected reactive functional groups such as −OH and −NH$_2$ (entries 4, 7, 10, and 13) also proved to be successful. Similarly, the corresponding products (**3s−3n**) from reaction of aliphatic thiols with epoxides were obtained with high yields (entries 19−22).

Under further observation, we examined the reactivity of heterocyclic thiols in the presence of Ga(OTf)$_3$ (entries 10 and 14). However, the reactions gave the products (**1j**, **1n**) in moderate yields under solvent-free conditions due to poor solubility of heterocyclic thiols in epoxides. Thus, the yields showed significant improvement when the reaction was run in CH$_3$NO$_2$.

Moreover, to extend the scope of this reaction, the thiolysis of chiral epoxides [(R)-epichlorohydrin (99% ee) or (S)-epichlorohydrin (98% ee)] was also examined using the present protocol. It is noteworthy that optically pure epoxides were converted into the corresponding β-hydroxy sulfides (**1o**, **1p**) without any racemization or inversion (entries 15 and 16).

Next, we reported one-pot synthesis of β-hydroxy sulfoxides via ring-opening and oxidation reactions starting from epoxides and thiophenols using H$_2$O$_2$ in the presence of Ga(OTf)$_3$.

First, the efficacy of various Lewis acids was investigated in the model reaction.[14b] The results showed that Ga(OTf)$_3$ was superior with respect to the amount of catalysts, reaction times, and product yields. In this case, only trace product was obtained after 24 h in the absence of Ga(OTf)$_3$. Although the reactions also proceeded with other metal triflates, long reaction times were required to achieve yields comparable to those obtained with Ga(OTf)$_3$.

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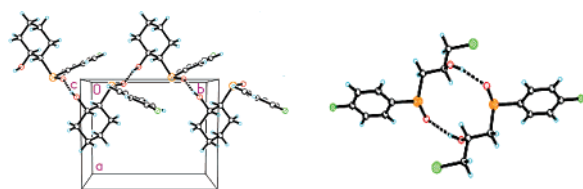
FIGURE 1. Intermolecular hydrogen bonds of **3c** and **3j** are indicated by dashed lines.

Interestingly, when Bi(OTf)₃ was used, diphenyldisulfide was formed contaminated by some overoxidation product β-hydroxy sulfone **4a**. The structure of **4a** was established by its X-ray single-crystal diffraction analysis.[15a] Only diphenyldisulfide was observed in 46% isolated yield after 12 h in the presence of Sc(OTf)₃. We supposed that it was due to oxidation coupling of thiophenol that converted it into diphenyldisulfide under these conditions. However, the reaction occurred with absolute chemoselectivity for formation of **3a** without any detectable overoxidation to **4a** in the presence of Ga(OTf)₃.[16] We next planned to determine the influence of solvent on the catalytic property of the reaction of cyclohexene oxide with thiophenol. Obviously, the presence of organic co-solvents did not make the reaction rate faster. Therefore, we chose to perform this reaction under sole water without any organic co-solvents.

To evaluate the scope of the catalyst's application, various epoxides were treated with thiophenols or thiols using H₂O₂ in the presence of 1 mol % of Ga(OTf)₃, and the results presented in Table 2 indicated that H₂O₂−Ga(OTf)₃-catalyzed one-pot reactions proceeded smoothly and produced the corresponding β-hydroxy sulfoxides in good to excellent yield. The corresponding β-hydroxy sulfoxides were afforded efficiently when less nucleophilic thiophenols such as *p*-fluorothiophenol were used. Electron-rich thiophenols such as *p*-methylthiophenol afforded the corresponding product in high yield as well (entry 2). Moreover, we also examined the reaction of aliphatic thiols with epoxides. Similarly, the corresponding products **3l** and **3m** were obtained with high yields (entries 12 and 13). On the other hand, we investigated the diastereoisomeric ratio of β-hydroxy sulfoxides by HPLC. Diastereoisomers of **3a** were isolated successfully by TLC; however, diastereoisomers of other β-hydroxy sulfoxides could not be isolated. The structures of **3c**[15b] and **3j**[15c] (entries 3 and 10) were established by their X-ray single-crystal diffraction analysis. As shown in Figure 1, the formation of the strong intermolecular hydrogen bond could greatly decrease the nucleophilicity at the sulfur atom.[15]

Using the H₂O₂−Ga(OTf)₃ system, the chemoselectivity was noteworthy. The sulfide function was highly reactive, and various functional groups, including C−C and −OH, were tolerable and were cleanly converted to β-hydroxy sulfoxides without epoxidation and dehydrogenation in almost excellent yields. Additionally, the present protocol followed an environmentally benign process in which the solid products were obtained through simple filtration in sole water media.

Finally, we also investigated the oxidation reactions of pure β-hydroxy sulfides (**1h**, **1i**), which were prepared before. The same results were obtained. However, the poor yields (12−14%)

were obtained in the absence of Ga(OTf)₃, which also further proved that Ga(OTf)₃ does play an important role in the oxidation reaction of β-hydroxy sulfides (entries 1 and 3).

In summary, we have developed a novel catalytic approach to the selective synthesis of β-hydroxy sulfides and β-hydroxy sulfoxides using a recyclable gallium(III) triflate. Obviously, the advantages of this method include (1) using a catalytic amount of Ga(OTf)₃ in high yields; (2) the catalyst could be recovered by simple extraction and reused several times; (3) The H₂O₂−Ga(OTf)₃ system of catalyzed reactions is a simple and environmentally benign procedure. Currently, studies on the extension of this protocol are ongoing in our laboratory.

Experimental Section

General Procedure for the Synthesis of β-Hydroxy Sulfides 1a−1v. To a mixture of epoxides (5 mmol) and thiophenols (5 mmol) was added Ga(OTf)₃ (0.05 mmol, 1 mol %). The mixture was stirred at 30 °C for 30 min. The progress of the reaction was monitored by TLC or HPLC. After completion of the reaction, water was added and the product was extracted with diethyl ether (3 × 10 mL). The organic layer was dried (MgSO₄) and evaporated, and the crude product was purified by flash chromatography (ethyl acetate/hexane, 1:15 to 1:5) to provide the corresponding products. The catalyst in the aqueous phase was concentrated in vacuo to give a crystalline residue, which was finally heated at 180 °C for 48 h in vacuo to afford Ga(OTf)₃ as colorless crystal. The recovered Ga(OTf)₃ could be reused in the next batch reaction.

General Procedure for One-Pot Synthesis of β-Hydroxy Sulfoxides 3a−3m. Method A: To a mixture of epoxides (5 mmol) and thiophenols (5 mmol) were added Ga(OTf)₃ (0.05 mmol, 1 mol %) and 1.2 mL of H₂O₂ (30 wt % aq solution, 10 mmol) and stirred at 30 °C. **Method B:** A mixture of epoxides (5 mmol), thiophenols (5 mmol), and Ga(OTf)₃ (0.05 mmol, 1 mol %) was stirred at 30 °C. After the ring-opening reaction was completed, 1.2 mL of H₂O₂ (30 wt % aq solution, 10 mmol) was added. Then the mixture was continuously stirred at 30 °C. The progress of the reaction was monitored by TLC or HPLC. After completion of the reaction, the excess amount of H₂O₂ was destroyed by the addition of a saturated aqueous solution of Na₂SO₃ to the reaction mixture. If the products are solid, they were obtained through simple filtering which did not need further purification. If the products are liquid, the reaction mixture was extracted with diethyl ether (3 × 10 mL). The organic layer was dried (MgSO₄) and evaporated, and the crude product was purified by flash chromatography to provide the products. Selected data: **3k**: oil, R_f = 0.2 (petroleum ether/EtOAc = 1:1); ¹H NMR (300 MHz, CDCl₃) δ 7.68−7.63 (m, 2H, ArH), 7.58−7.53 (m, 3H, ArH), 5.84−5.73 (m, 1H, CH₂ = C*H*−C), 5.00−4.90 (m, 2H, C*H₂* = C), 4.32−4.30 (m, 1H, C*H*OH), 3.04−2.70 (m, 3H, C*H₂*S(O) and OH), 2.06−1.99 (m, 2H, CH₂ = CH−C*H₂*), 1.58−1.25 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 143.8, 138.9, 131.3, 129.4, 123.9, 68.7, 62.3, 36.9, 33.7, 29.1, 28.8, 28.6, 24.8; IR ν_max 3373, 2927, 2855, 1444, 1020 (SO st) cm⁻¹; MS (EI) *m/z* 281 (M⁺ + 1, 85), 263 (42), 126 (100). Anal. Calcd for C₁₆H₂₄O₂S: C, 68.53; H, 8.63. Found: C, 68.48; H, 8.71.

Supporting Information Available: General experimental details, X-ray crystal structure, and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) See Supporting Information: (a) Table 1; (b) Table 2.

(15) (a) CCDC-614766; (b) CCDC-614633; (c) CCDC-614765 contains the supplementary crystallographic data, which is available free of charge via www.ccdc.cam.ac.uk.

(16) The t_R (**4a**) and t_R (**3a**) showed the obvious difference in the same conditions (see Supporting Information).