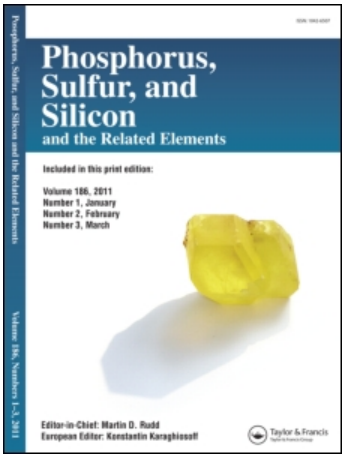

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$BiCl_3$ Catalyzed Thiolyzation Reaction of 1,2-Epoxides with Diaryl Disulfides in the Presence of Zinc Powder and Ionic Liquid

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A new and efficient method has been developed for the regio- and chemoselective synthesis of β-hydroxysulfides with the ring-opening reaction of 1,2-epoxides by diaryl disulfides and zinc powder in the presence of a catalytic amount of $BiCl_3$ in molten tetrabutyl phosphonium bromide as an ionic liquid.

Keywords β-hydroxysulfides; aryl disulfides; $BiCl_3$; epoxides; ionic liquid; ring opening reaction

INTRODUCTION

In recent years, β-hydroxysulfide derivatives have attracted considerable interest due to their wide utilization in organic synthesis for the preparation of benzoxathiepines,[1] benzotiazepines,[2] β-hydroxysulfoxides,[3] or α-thioketones,[4] which are versatile in the realm of pharmaceutical, biological, or organic chemistry. Thus, the synthesis of this heterochemical system is of much interest. One of the classical synthetic methods for the preparation of β-hydroxysulfides consists of a ring opening of an epoxide with an excess of thiol.[5] Because some functional groups may be sensitive to high temperature, some modified methods have been developed.[6] However, many of these procedures are associated with one or more disadvantages, such as involving toxic and expensive catalysts or hazardous and carcinogenic organic solvents for reactions. In addition, low yields, long reaction times, and the utilization of large amounts of catalyst or solvent limit these synthetic scopes

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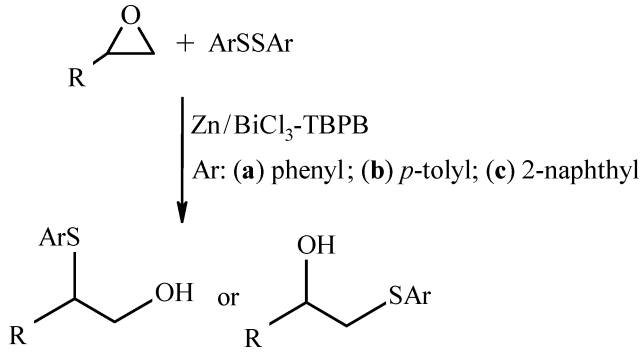
to small scales. Hence, a simple, green, and efficient procedure avoiding these drawbacks that leads to convenient procedures and better yields is recommended.

RESULTS AND DISCUSSION

The toxic and volatile nature of many organic solvents have posed a serious threat to the environment. Consequently, methods that minimize their use are the focus of much attention. In this respect, ionic liquids are attracting a growing interest as an alternative reaction media for various chemicals and biotransformations.[7] These compounds offer an alternative and ecologically friendly media that, in contrast to organic solvents, are nonvolatile and non-explosive.[8] On the other hand, the catalysts that have polar or ionic character can be immobilized without additional structural modification, and thus, the ionic solutions containing the catalyst easily can be separated from products. Thus, ionic liquids have proven to be excellent solvents for many organic reactions.[9]

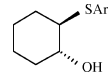
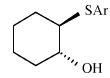
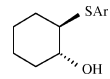
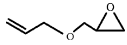
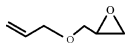
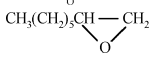
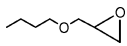
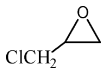
Most bismuth (III) salts are relatively nontoxic, easy to handle, and can tolerate small amounts of moisture.[10] With increasing environmental concerns and the need for green reagents, the interest in bismuth (III) salts has increased tremendously in the last decade.[11] In continuation of our studies using Bi(III) salts for various organic transformations,[12] we wish to present a new and convenient method for the synthesis of β-hydroxysulfides toward the ring opening of epoxides with diaryl disulfides and zinc powder catalyzed by $BiCl_3$ that is immobilized on molten tetrabutylphosphonium bromide (TBPB) as an ionic liquid (Scheme 1).



SCHEME 1

The experimental procedure is very simple. To the mixture of molten TBPB and $BiCl_3$, zinc powder, diaryl disulfide and 1,2-epoxide were

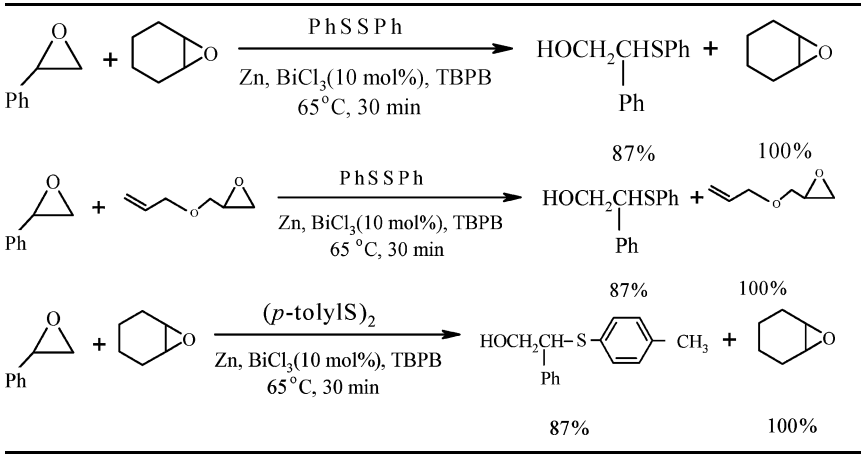
TABLE I Ring Opening of 1,2-Epoxides With ArSSAr in the Presence of Zinc Powder and 10 mol% of $BiCl_3$ in the Presence of Molten TBPB

Entry	Epoxide	Ar	Yield (%)[a]/ Time(min)	Product
1		Ph	92/20	$OHCH_2CH(Ph)-SAr$
2		*P*-$CH_3C_6H_4$	92/20	$OHCH_2CH(Ph)-SAr$
3		2-Naphthyl	88/25	$OHCH_2CH(Ph)-SAr$
4		Ph	80/60[b]	
5		*P*-$CH_3C_6H_4$	80/45[b]	
6		2-Naphthyl	78/65[b]	
7		Ph	89/40	$PhOCH_2CH(OH)CH_2-SAr$
8		*P*-$CH_3C_6H_4$	90/45	$PhOCH_2CH(OH)CH_2-SAr$
9		Ph	80/65	$CH_2=CHCH_2OCH_2CH(OH)CH_2-SAr$
10		*P*-$CH_3C_6H_4$	80/65	$CH_2=CHCH_2OCH_2CH(OH)CH_2-SAr$
11		Ph	86/30	$CH_3(CH_2)_5CH(OH)CH_2-SAr$
12		Ph	90/60	$CH_3(CH_2)_2CH_2OCH_2CH(OH)CH_2-SAr$
13		Ph	86/55	$ClCH_2CH(OH)CH_2-SAr$

[a]Isolated yields.
[b]In the presence of 20 mol% of $BiCl_3$.

added and the system was stirred at 65°C and the product was isolated by usual work-up. The results are summarized in Table I. In the method described here, a variety of epoxides with different functional groups such as PhO-, RO-, $ClCH_2$-, and allyl ether were converted to the products with high efficiency and chemoselectivity. It is important to note that in the case of terminal epoxides (Table I, entries 7–13), the products were obtained by the attack of nucleophiles on the terminal carbon. This regioselectivity is probably due to the steric hinderance of nucleophile that attacks on the less-hindered carbon of the epoxides.

TABLE II Competetive Ring Opening Reaction of 1,2-Epoxides With Diaryl Dosulfides in the Presence of Zinc Powder and $BiCl_3$ in the Presence of Molten TBPB



However, in the case of the reaction with styrene oxide, we observed a reverse regioselectivity in which the attack on the benzylic carbon (which may be due to the formation of more stable carbocation on benzylic carbon) was preferred (Table I, entries 1–3). The products that were obtained using cyclohexene oxide posses a *trans*-configuration by ^{1}H NMR spectroscopy (Table I, entries 4–6). This high reactivity and selectivity is similar to those observed in the case of strong Lewis acids with thiophenols.[6] On the other hand, we found that aliphatic disulfides such as dibenzyl disulfide or dicyclohexyl disulfide are quite resistant to the reaction conditions and completely recovered.

In order to evaluate the intermolecular chemoselectivity of the reagents, we also examined the competitive reactions (Table II). It is noteworthy that high chemoselectivity was exhibited with styrene oxide and the corresponding β-hydroxysulfide that was obtained in the presence of the other epoxides. In this competitive reaction, other acid-sensitive epoxides such as cyclohexane oxide in the presence of styrene oxide were stable.

CONCLUSIONS

In conclusion, we have demonstrated a new, efficient, and green catalytic procedure for the regio- and chemoselective thiolysation of 1,2-epoxides with diaryl disulfides in the ionic liquid media. In addition,

the ease of availability and low toxicity of the catalyst and the ionic liquid make this procedure environmentally acceptable. Furthermore, the low cost of the catalyst and ionic liquid, the high catalytic nature of the Lewis acid, and fast reaction rates make the present procedure a practical protocol for the β-hydroxysulfide synthesis.

EXPERIMENTAL

All yields refer to isolated products. The products were characterized by comparison with authentic samples.[6] All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 200 MHz spectrophotometer in $CDCl_3$ as a solvent. Diaryl disulfides were prepared according to the literature.[13]$BiCl_3$-TBPB was prepared by mixing $BiCl_3$ (0.1–0.2 mmol) and molten tetrabutylphosphonium bromide (0.5 mmol), which heated to 120°C, then this mixture cooled to 65°C.

General Procedure for the Ring Opening Reaction of 1,2-Epoxides With Diaryl Disulfides in the Presence of Zinc Powder Catalyzed by $BiCl_3$-TBPB

In a 50 mL round bottom, 1,2-epoxide (1 mmol), diaryl disulfide (1 mmol), and zinc powder (1 mmol) were added to a molten mixture of tetrabutylphosphonium bromide (0.5 mmol) and $BiCl_3$ (0.1–0.2 mmol), then the reaction mixture stirred at 65°C for the appropriate times (Table I). The progress of the reaction was followed by TLC (n-heptane/ethyl acetate: 3/1). After completion of the reaction, Et_2O (20 mL) was added and the mixture was filtered. The evaporation of the organic layer gave the corresponding crude products, which were purified by chromatography on a silica-gel plate to afford the pure β-hydroxythioethers in 78–92% yields. Spectroscopy data: Product of entry **1**. IRν_{max} cm^{-1}: 3370, 3005, 2895, 2860, 1585, 1465, 1050, 740, 695 (neat). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.15–7.55 (m, 10H), 4.35 (t, J 6.8 Hz, 1H), 3.95 (d, J 6.8 Hz, 2H), 2.10 (s, 1H).^{13}C NMR (50 MHz, $CDCl_3$) δ 139.40, 134.20, 132.90, 129.40, 129.20, 128.50, 128.20, 128.00, 65.70, 56.50. Product of entry **2**. IR ν_{max} cm^{-1}: 3430, 3015, 2905, 2880, 1590, 1495, 1440, 1060, 850, 735, 690 (neat). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50–7.90 (m, 9H), 4.75 (t, J 6.9 Hz, 1H), 4.35 (d, J 6.9 Hz, 2H), 2.80 (s, 4H).^{13}C NMR (50 MHz, $CDCl_3$) δ 139.60, 138.30, 133.70, 130.30, 130.20, 129.10, 128.60, 128.20, 65.50, 56.80, 21.60. Product of entry **3**. IR ν_{max} cm^{-1}: 3520, 3030, 2905, 2890, 1595, 1490, 1450, 1090, 850, 730, 695 (neat). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30–7.95 (m, 12H,), 4.52 (t, J 8.0 Hz, 1H), 4.05 (d, J 7.0 Hz, 2H), 2.25 (s, 1H).^{13}C NMR (50 MHz, $CDCl_3$) δ 139.30, 133.90, 132.80, 131.80, 131.50, 130.10, 129.20, 128.90, 128.60,

128.30, 128.10, 127.90, 127.00, 126.80, 65.70, 56.40. Product of entry **4**. IR ν_{max} cm^{-1}: 3650, 3015, 2905, 2885, 1590, 1495, 1440, 1065, 840, 735, 690 (neat). ^1H NMR (200 MHz, $CDCl_3$) δ 7.25–7.60 (m, 5H), 3.30–3.50 (m, 1H), 2.90 (s, 1H), 2.70–2.85 (m, 1H), 2.05–2.25 (m, 2H), 1.62–1.83 (m, 2H), 1.20–1.50 (m, 4H).^{13}C NMR (50 MHz, $CDCl_3$) δ 134.20, 133.00, 129.30, 128.20, 72.40, 56.90, 34.20, 33.10, 26.60, 24.70. Product of entry **5**. IR ν_{max} cm^{-1}: 3450, 3010, 2900, 2880, 1590, 1495, 1450, 1060, 820 (neat). ^1H NMR (200 MHz, $CDCl_3$) δ 7.85 (d, J 10.0 Hz, 2H), 7.55 (d, J 10.0 Hz, 2H), 3.70–3.85 (m, 1H), 3.55 (s, 1H), 3.10–3.25 (m, 1H), 2.8 (s, 3H), 2.50–2.65 (m, 2H), 2.05–2.20 (m, 2H), 1.10–1.60 (m, 4H).^{13}C NMR (50 MHz, $CDCl_3$) δ 138.50, 134.90, 130.10, 128.90, 72.20, 56.90, 34.20, 32.90, 26.60, 24.70, 21.60. Product of entry **6**. IR ν_{max} cm^{-1}: 3440, 3020, 2905, 2885, 1595, 1490, 1440, 1085, 810 (neat). ^1H NMR (200 MHz, $CDCl_3$) δ 7.50–8.10 (m, 7H), 3.40–3.60 (m, 1H), 2.90–3.05 (m, 2H), 2.10–2.25 (m, 2H), 1.70–1.90 (m, 2H), 1.15–1.60 (m, 4H).^{13}C NMR (50 MHz, $CDCl_3$) δ 133.90, 133.30, 132.90, 131.50, 130.30, 128.90, 128.10, 127.90, 127.00, 126.90, 72.50, 57.00, 34.30, 33.20, 26.60, 24.70. Product of entry **7**. IR ν_{max} cm^{-1}: 3400, 3010, 2900, 2880, 1590, 1480, 1245, 1050, 730, 695 (neat). ^1H NMR (200 MHz, $CDCl_3$) δ 7.85–7.70 (m, 10H), 3.95–4.25 (m, 3H), 3.10–3.40 (m, 2H), 2.75 (s, 1H).^{13}C NMR (50 MHz, $CDCl_3$) δ 158.80, 135.60, 130.25, 130.00, 129.60, 127.10, 121.70, 115.00, 70.50, 69.00, 38.00. Product of entry **9**. IR ν_{max} cm^{-1}: 3350, 3020, 2905, 2880, 1600, 1490, 1380, 1060, 735, 690 (neat). ^1H NMR (200 MHz, $CDCl_3$) δ 7.15–7.50 (m, 5H), 5.80–6.05 (m, 1H), 5.15–5.35 (m, 2H), 4.00 (d, J = 6.8 Hz, 2H), 3.80–3.95 (m, 1H), 3.45–3.65 (m, 2H), 3.00–3.25 (m, 2H), 2.70 (s, 1H).^{13}C NMR (50 MHz, $CDCl_3$) δ 135.90, 134.80, 130.10, 129.50, 126.90, 117.80, 72.80, 72.70, 69.40, 37.90. Product of entry **10**. IR ν_{max} cm^{-1}: 3700, 3015, 2905, 2885, 1590, 1495, 1440, 1080, 790 (neat). ^1H NMR (200 MHz, $CDCl_3$) 7.75 (d, J = 8.0 Hz, 2H), δ 7.55 (d, J 8.0 Hz, 2H), 6.20–6.45 (m, 1H), 5.60–5.80 (m, 2H), 4.40 (d, 2H), 4.25–4.35 (m, 1H), 3.90–4.10 (m, 2H), 3.35–3.65 (m, 2H), 3.20 (s, 1H), 2.80 (s, 3H).^{13}C NMR (50 MHz, $CDCl_3$) δ 137.10, 134.80, 132.10, 130.90, 130.20, 117.70, 72.80, 72.70, 69.30, 38.70, 21.40. Product of entry **11**. IR ν_{max} cm^{-1}: 3405, 3015, 2905, 2880, 1585, 1490, 1435, 735, 690 (neat). ^1H NMR (200 MHz, $CDCl_3$) δ 7.15–7.50 (m, 5H), 3.50–3.80 (m, 1H), 3.10–3.25 (dd, J 4.5 Hz, J 4.5 Hz, 2H), 2.80–2.95 (dd, J 9.5 Hz, J 9.5 Hz, 2H), 2.70(s, 1H), 1.15–1.70 (m, 8H), 0.95 (t, J 7.0 Hz, 3H).^{13}C NMR (50 MHz, $CDCl_3$) δ 136.00, 130.30, 130.00, 126.90, 69.90, 42.50, 36.60, 32.20, 29.60, 26.10, 23.00, 14.50. Product of entry **12**. IR ν_{max} cm^{-1}: 3410, 3025, 2900, 2890, 1590, 1490, 1430, 735, 690 (neat). ^1H NMR (200 MHz, $CDCl_3$) δ 7.15–7.50 (m, 5H), 3.85–4.00 (m, 1H), 3.40–3.65 (m, 4H), 3.00–3.25 (m, 2H), 2.80 (s, 1H), 1.55–1.70 (m, 2H), 1.30–1.50 (m, 2H), 0.95 (t, J 8.3 Hz, 3H).^{13}C NMR (50 MHz, $CDCl_3$) δ 136.10, 129.90, 129.40, 126.70, 73.70,

71.70, 69.40, 37.80, 32.10, 19.70, 14.30. Product of entry **13**. IR ν_{max} cm^{-1}: 3425, 3010, 2920, 2830, 1600, 1490, 1430, 1365, 1110, 740, 690 (neat). ^1H NMR (200 MHz, $CDCl_3$) δ 7.20–7.50 (m, 5H), 3.90–4.10 (m, 1H), 3.72 (d, J = 8.0 Hz, 2H), 3.05–3.18 (m, 2H), 2.88 (s, 1H).^{13}C NMR (50 MHz, $CDCl_3$) δ 135.10, 130.50, 129.70, 127.30, 69.90, 48.40, 38.60.

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