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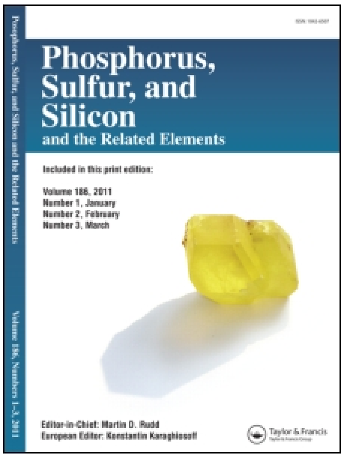

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The Green Method for Regiospecific Ring Opening of Epoxide with Dimercaptoethane

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The Green Method for Regiospecific Ring Opening of Epoxide with Dimercaptoethane

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A simple, efficient, and environmentally friendly one-step regiospecefic ring opening of strained epoxides with dimercaptoethane as a nucleophile in nearly saturated aqueous potassium carbonate is reported. The synthesized β,β'*-dihydroxydithioether compounds were confirmed by elemental analysis,* ^{1}H *NMR,* ^{13}C *NMR, and MS spectral studies.*

INTRODUCTION

The ring opening of epoxides[1] with various nucleophils is an important synthetic transformation in organic chemistry. The preparation of β-hydroxy thioethers is generally realized by the action of thiolates[2] or thiols in the presence of metal salts such as Lanthanum[3], Cobalt,[4] Titanium[5], complex of Gallium-Lithium *bis*-naphtoxide[6] and Lewise acids $ZnCl_2$,[7] and $InCl_3$.[8] Ring opening reaction by thiols was also carried out in the presence of alumina[9] and polyethylene glycol.[10] This reaction has also been reported in hexafluoroisopropanol without using catalyst.[11] The ring opening of oxiranes with dimercaptoethane has been recently performed in the presence of benzyltrimethylammonium hydroxide (Triton B) as catalyst.[12] Highly regioselective ring opening of epoxides by thiophenols in ionic liquids has also been reported.[13] Herein, we report the ring opening reaction of two mole equivalents of epoxides with dimercaptoethane in saturated aqueous solution of potassium carbonate to prepare corresponding β,β'-dihydroxy dithioethers. Having two secondary hydroxy groups, make these compounds susceptible reagents to synthesize new thiocrown ethers possessing various sidearms.[14]

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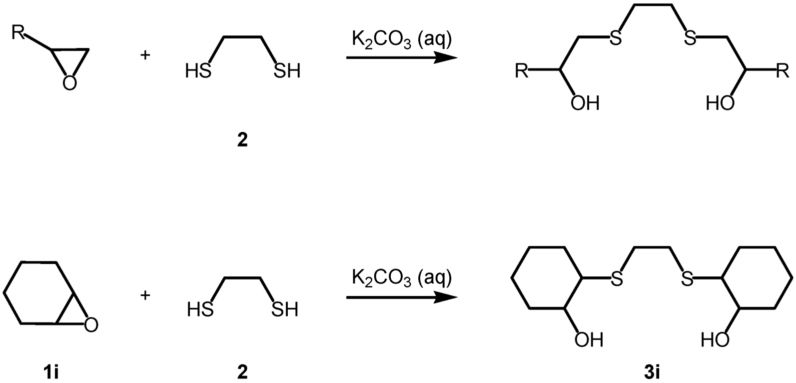
Many efforts are developed to perform chemical reactions in aqueous media to safe environmental conditions.[15] Water is cheap, readily available, and nontoxic, resulting in an economic process that has clear advantages as an environmentally friendly solvent alternative in organic synthesis.[16]

RESULTS AND DISCUSSION

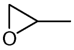
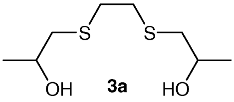
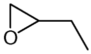
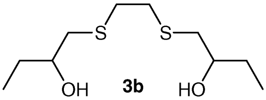
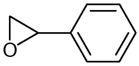
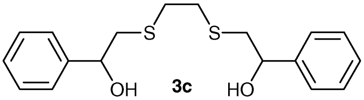
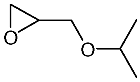
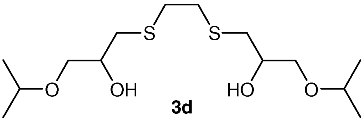
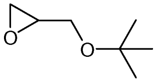
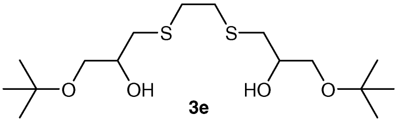
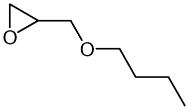
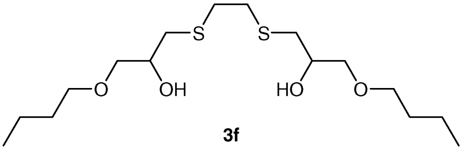
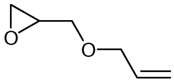
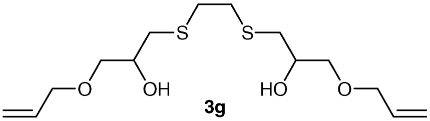
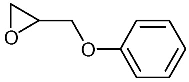
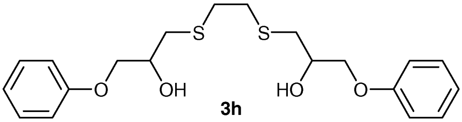
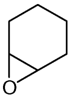
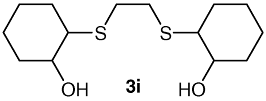
The ring opening of the starting epoxides (**1a–i**) was regionspecific by nucleophilic attack on the terminal carbon atoms affording a secondary diols. The water solubility of epoxides are decreased in the presence of high concentrations of potassium carbonate lead to decrease epoxide ring opening percentage by the protic solvent.[17] Dimercaptoethan is deprotonated by carbonate anion (rather than water deprotonation) lead to formation of water soluble dimercaptid anion, which can react with epoxides in the boundary surface of aqueous and organic phase. This is a suitable condition of the S_N2 mechanism resulted nucleophilic attack on low substituted site.[17] Obviously, the ring opening of epoxides (**1a–i**) afforded corresponding dihydroxy dithioethers as a mixture of isomeric diastreomers.[12] It was notable that in low concentrations of potassium carbonate, the formation of monosubstituted ethandiols—instead of formation of corresponding β,β'-dihydroxydithioethers—was increased. This was obvious when the results were checked by TLC and sodium metaperiodate-benzidine test of 1,2-diols.[18]

The β,β'-dihydroxydithioethers (**3a–i**) were prepared by the action of two mole equivalents of epoxides (**1a–i**) with deporotonated dimercaptoehane (**2**), which was formed by proton abstracting of carbonate anion under reflux condition and vigorous stirring (Scheme 1). All



SCHEME 1

TABLE I Thiolysis by Dimercaptoethane of Epoxides (1a–i) in Aqueous Potassium Carbonate to Give Beta, Beta′-dihydroxy Dithioether

Epoxides	Beta, Beta′-dihydroxy Dithioether	Time (hour)	Yield (%)
1a 	 **3a**	5	94
1b 	 **3b**	4	97
1c 	 **3c**	3	91
1d 	 **3d**	3	96
1e 	 **3e**	3	96
1f 	 **3f**	3	96
1g 	 **3g**	3	99
1h 	 **3h**	3	96
1i 	 **3i**	3	89

dihydroxy compounds were obtained in excellent (Table I) and indicated high regioselectivity by showing one spot on TLC, which did not need further purification. The dihydroxy compounds (**3a–g**) were isolated by decanting and (**3h–i**) by filtering follow by washing with water.

CONCLUSION

The method used here is a simple, efficient, and environmentally friendly procedure with excellent yields, high regioselectivity, and no need for any organic solvents either for reaction medium or extracting the products. Therefore, the work follows the basic aims which are important to green chemistry.[19]

EXPERIMENTAL

Melting points were recorded on an Electrothermal type 9100 melting point apparatus. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were obtained by using a Bruker Avance DRX-500 Fourier transformer spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane (TMS). Electron impact (EI) mass spectra were recorded on a Varian Match 7A spectrometer. Elemental analysis was obtained on a Thermo Finnigan Flash EA microanalyzer. All chemicals were purchased from Merck and Fluka Co. and used without further purification.

General Procedure for Ring Opening of Epoxides 1a-i with Dimercaptoethane (2)

To a solution of potassium carbonate (50 g, 350 mmol) in water (65 ml) was added dimercaptoethane (**2**) (13.5 ml, 160 mmol) followed by epoxide (300 mmol). The mixture was refluxed in oil bath while stirring vigorously. The completion of reaction was checked by TLC (silica gel 60 F_{254}, benzene-ethylacetate 50:50).

After completion, the mixture was cooled, and the precipitated products (**3h–i**) were filtered, washed with water (3 × 50 ml), and dried in oven at 50–55° for 4h. The liquid products (**3a–g**) in aqueous phase were decantated, washed with water (3 × 50 ml), and then heated in oven at 80–90° for 2h to eliminate water. The remainder of the carbonate solution was reused in subsequent runs.

1-(2-[(2-Hydroxypropyl)sulfanyl]ethylsulfanyl)-2-propanol 3a

Colorless oil (Found: C, 45.91; H, 8.57; S, 30.27. $C_8H_{18}O_2S_2$ requires C, 45.68; H, 8.62; S, 30.49%); δ_H 1.25 (6H, d, *J* 6.3, 2 × CH_3), 2.51 (2H, dd, *J* 8 and 20, 2 × CH_2S), 2.73 (2H, dd, *J* 4.1 and 12.5, 2 × CH_2S), 2.78 (4H, s, SCH_2CH_2S), 2.92 (2H, br, 2 × OH), 3.87 (2H, m, 2 × CH); δ_C 21.96 (2 × q), 32.41 (2 × t), 41.40 (2 × t), 65.92 (2 × d); *m/z* EI 210 (M^+), 165 (12%) $C_6H_{13}OS_2$, 151 (58) $C_5H_{11}OS_2$, 119 (65) $C_5H_{11}OS$, 75 (100) C_3H_7S.

1-(2-[(2-Hydroxybutyl)sulfanyl]ethylsulfanyl)-2-butanol 3b

Colorless oil (Found: C, 50.20; H, 9.34; S, 26.82. $C_{10}H_{22}O_2S_2$ requires C, 50.38; H, 9.30; S, 26.90%); δ_H 0.97 (6H, t, *J* 7.5, 2 × CH_3), 1.54 (4H, m, 2 × CH_3CH_2), 2.52 (2H, dd, *J*8 and 20, 2 × CH_2S), 2.75 (2H, dd, *J*4.1 and 12.5, 2 × CH_2S), 2.78 (4H, s, SCH_2CH_2S), 2.93 (2H, br, 2 × OH), 3.61 (2H, m, 2 × CH); δ_C 9.82 (2 × q), 28.87 (2 × t), 32.24 (2 × t), 39.46 (2 × t), 71.02 (2 × d); *m/z* EI 238 (M^+), 179 (18%) $C_7H_{15}OS_2$, 133 (94) $C_6H_{13}OS$, 105 (95) C_4H_9OS, 75 (100) C_3H_7S.

2-(2-[(2-Hydroxy-2-phenylethyl)sulfanyl]ethylsulfanyl)-1-phenyl-1-ethanol 3c

Colorless oil (Found: C, 64.68; H, 6.57; S, 19.09. $C_{18}H_{22}O_2S_2$ requires C, 64.63; H, 6.63; S, 19.17%); δ_H 2.55-2.93 (4H, m, 4 × CH_2S), 2.76 (4H, s, SCH_2CH_2S), 3.45 (2H, br, 2 × OH), 4.74 (2H, m, 2 × CH), 7.37 (10 H, m, 2 × Ph); δ_C 32.63 (2 × t), 42.78 (2 × t), 77.65 (2 × d), 128.74 (2 × d), 130.02 (d), 130.88 (2 × d), 139.84 (d); *m/z* EI 334 (M^+), 317 (11%) $C_{18}H_{21}OS_2$, 227 (23) $C_{11}H_{15}OS_2$, 213 (28) $C_{10}H_{13}OS_2$, 196 (72) $C_{10}H_{12}S_2$, 136 (92) $C_4H_8OS_2$, 121 (96) C_8H_9O, 107 (100) C_7H_7O.

1-(2-[(2-Hydroxy-3-isopropoxypropyl)sulfanyl]ethylsulfanyl)-3-isopropoxy-2-propanol 3d

Colorless oil (Found: C, 51.43; H, 9.21; S, 19.39. $C_{14}H_{30}O_4S_2$ requires C, 51.50; H, 9.26; S, 19.64%); δ_H 1.21 (12H, d, *J* 6.1, 2 × CH_3CHCH_3) 2.69 (2H, dd, *J*7 and 19.5, 2 × CH_2S), 2.77 (2H, dd, *J*5.2 and 17.4, 2 × CH_2S), 2.84 (4H, s, SCH_2CH_2S), 2.92 (2H, br, 2 × OH), 3.47 (2H, dd, *J* 6.3 and 15.7, 2 × CH_2O), 3.55 (2H, dd, *J* 4.1 and 13.5, 2 × CH_2O), 3.65 (2H, m, 2 × CH_3CHCH_3), 3.90 (2H, m, 2 × CH); δ_C 22.45 (2 × q), 32.99 (2 × t), 36.14 (2 × t), 67.05 (2 × d), 71.02 (2 × t), 72.75 (2 × t); *m/z* EI 326 (M^+), 297 (11%) $C_{12}H_{25}O_4S_2$, 209 (48) $C_8H_{17}O_2S_2$, 177 (57) $C_8H_{17}O_2S$, 103 (88) $C_5H_{11}O_2$, 59 (100) C_3H_7O.

1-(Tert-butoxy)-3-[(2-[3-(tert-butoxy)-2-hydroxypropyl] sulfanylethyl)sulfanyl]-2-propanol 3e

Colorless oil (Found: C, 54.43; H, 9.71; S, 17.98. $C_{16}H_{34}O_4S_2$ requires C, 54.20; H, 9.67; S, 18.09%); δ_H 1.18 (18H, s, 2 × C_4H_9), 2.68 (2H, dd, *J*7 and 19.5, 2 × CH_2S), 2.76 (2H, dd, *J*5.2 and 17.4, 2 × CH_2S), 2.83 (4H, s, SCH_2CH_2S), 2.87 (2H, br, 2 × OH), 3.46 (2H, dd, *J* 6.3 and 15.7, 2 × CH_2O), 3.54 (2H, dd, *J* 4.1 and 13.5, 2 × CH_2O), 3.86 (2H, m, 2 × CH); δ_C 27.45 (2 × q), 33.09 (2 × t), 36.24 (2 × t), 67.76 (2 × d), 71.62 (2 × t), 73.15 (2 × t); *m/z* EI 354 (M^+), 223 (53%) $C_9H_{19}O_2S_2$, 166 (54) $C_5H_{10}O_2S_2$, 137 (60) $C_4H_9OS_2$, 57 (100) C_4H_9.

1-Butoxy-3-(2-[(3-butoxy-2-hydroxypropyl)sulfanyl] ethylsulfanyl)-2-propanol 3f

Colorless oil (Found: C, 54.16; H, 9.73; S, 18.22. $C_{16}H_{34}O_4S_2$ requires C, 54.20; H, 9.67; S, 18.09%); δ_H 0.89 (6H, t, *J*8, 2 × CH_3), 1.18–1.69 (8H, m, 2 × CH_2CH_2), 2.64 (2H, dd, *J*1.1, 7 and 19.5, 2 × CH_2S), 2.70 (2H, dd, *J*5.2 and 17.4, 2 × CH_2S), 2.76 (4H, s, SCH_2CH_2S), 2.90 (2H, br, 2 × OH), 3.42(2H, dd, *J* 6.3 and 15.7, 2 × CH_2O), 3.49 (2H, dd, *J* 4.1 and 13.5, 2 × CH_2O), 3.46 (4H, t, *J* 8, 2 × $CH_2\mathit{CH_2}O$), 3.87 (2H, m, 2 × CH); δ_C 14.44 (2 × q), 19.30 (2 × t), 31.2 (2 × t) 33.15 (2 × t), 36.08 (2 × t), 67.70 (2 × d), 71.53 (2 × t), 72.89 (2 × t); *m/z* EI 354 (M^+), 223 (43%) $C_9H_{19}O_2S_2$, 191 (63) $C_9H_{19}O_2S$, 57 (100) C_4H_9.

1-(Allyloxy)-3-[(2-[3-(allyloxy)-2-hydroxypropyl]sulfanylethyl) sulfanyl]-2-propanol 3g

Colorless oil (Found: C, 52.16; H, 8.18; S, 19.78. $C_{14}H_{26}O_4S_2$ requires C, 52.14; H, 8.13; S, 19.89%); δ_H 2.68 (2H, dd, *J*7.1 and 13.8, 2 × CH_2S), 2.76 (2H, dd, *J*4.2 and 17.8, 2 × CH_2S), 2.81 (4H, s, SCH_2CH_2S), 3.50 (2H, dd, *J* 6.2 and 15.9, 2 × CH_2O), 3.55 (2H, dd, *J* 4.1 and 13.7, 2 × CH_2O), 3.95 (2H, m, 2 × CH), 4.05 (4H, d, *J* 5.6, 2 × $CH_2=CH\mathit{CH_2}O$), 5.06 (2H, br, 2 × OH), 5.22 (2H, dd, *J* 10 and 1.2, 2 × $\mathit{CH_2}=CH$), 5.30 (2H, dd, *J* 17 and 1.2, 2 × $\mathit{CH_2}=CH$), 5.86–5.94 (2H, m, 2 × $CH_2=\mathit{CH}$); δ_C 33.06 (2 × t), 36.08 (2 × t), 69.33 (2 × d), 70.11 (2 × t), 72.77 (2 × t), 117.99 (2 × t), 134.68 (2 × d); *m/z* EI 322 (M^+), 247 (13%) $C_{10}H_{15}O_3S_2$, 207 (30) $C_8H_{15}O_2S_2$, 175 (54) $C_8H_{15}O_2S$, 147 (57) $C_6H_{11}O_2S$, 71 (62) C_4H_7O, 41 (100) C_3H_5.

1-(2-[(2-Hydroxy-3-phenoxypropyl)sulfanyl]ethylsulfanyl)-3-phenoxy-2-propanol 3h

White solid (Found: C, 61.13; H, 6.72; S, 16.07. $C_{20}H_{26}O_4S_2$ requires C, 60.88; H, 6.64; S, 16.25%); m.p. 79°C (from carbon tetrachloride); δ_H 2.39 (2H, br, 2 × OH), 2.71 (2H, dd, *J*7.2 and 15.5, 2 × CH_2S), 2.79 (2H, dd, *J*4.2 and 17.8, 2 × CH_2S), 2.85 (4H, s, SCH_2CH_2S), 4.04 (2H, dd, *J* 6.2 and 15.8, 2 × CH_2O), 4.12 (2H, m, 2 × CH), 4.15 (2H, dd, *J* 4.1 and 13.7, 2 × CH_2O), 6.84-7.38 (10 H, m, 2 × Ph); δ_C 33.10 (2 × t), 35.80 (2 × t), 69.91 (2 × t), 70.92 (2 × d), 114.90 (2 × d), 121.09 (d), 120.74 (2 × d), 159.23 (d); *m/z* EI 394 (M^+), 287 (85%) $C_{13}H_{19}O_3S_2$, 243 (86) $C_{11}H_{15}O_2S_2$, 211 (90) $C_{11}H_{15}O_2S$, 75 (100) C_6H_5.

2-(2-[(2-Hydroxycyclohexyl)sulfanyl]ethylsulfanyl)-1-cyclohexanol 3i

White solid (Found: C, 58.13; H, 9.06; S, 22.07. $C_{14}H_{26}O_2S_2$ requires C, 57.89; H, 9.02; S, 22.08%); m.p. 72°C (from carbon tetrachloride); δ_H 1.25–1.54 (8H, m, 2 × CH_2CH_2), 1.73 (4H, m, 2 × CH_2CHS), 2.08 (4H, m, 2 × CH_2CHOH), 2.33 (2H, br, 2 × OH), 2.27–2.44 (2H, m, 2 × CHS), 2.80 and 2.83 (4H, two singlets, 2 × SCH_2CH_2S), 317-3.41 (2H, m, 2 × CH); δ_C24.22 (2 × t), 26.03 (2 × t), 30.72 and 31.11 (two peaks, 2 × t), 32.87 and 32.97 (two peaks, 2 × t), 33.83 (2 × t), 53.33 and 53.42 (two peaks, 2 × d), 72.41 and 72.79 (two peaks, 2 × d); *m/z* EI 290 (M^+), 273 (10%) $C_{14}H_{25}OS_2$, 159 (94) $C_8H_{15}OS$, 99 (95) $C_6H_{11}O$, 83 (100) C_6H_{11}.

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