SUPPORTING INFORMATION

Zn(II)-Catalyzed Thiolytic of Oxiranes in Water under Neutral Conditions

Francesco Fringuelli, Ferdinando Pizzo, Simone Tortoioli, Luigi Vaccaro*

Università di Perugia, Dipartimento di Chimica, Via Elce di Sotto, 8 I-06100 Perugia, Italy.

E-mail: pizzo@unipg.it

List of CONTENTS of the Supporting Information:

- Page S1: Experimental Section.
- Page S2: characterizations of the compounds 2-(buthylthio)-1-methylciclohexanol, 2-(buthylthio)-2-methylciclohexanol.
- Page S3: characterizations of the compounds 6-(phenylthio)-hexan-1,5-diol, 1-(phenylthio)-3-[(trimethylsilyl)oxy]propan-2-ol and *anti*-1-(tosyloxy)-3-(phenylthio)-2-hexanol (**15**).
- Page S3: characterization of the compound *anti*-1,3-bis(phenylthio)hexan-2-ol (**16**).

Experimental section

General. All chemicals were purchased and used without any further purification. GC analyses were performed with an SPB-5 fused silica capillary column (30 m, 0.25 mm diameter), an “on column” injector system, an FID detector and hydrogen as the carrier gas. GC-MS analyses were carried out with 70 eV electron energy. Column chromatographies were performed on silica gel (0.040-0.063 mm). ¹H and ¹³C NMR spectra were recorded at 200 MHz and 50.3 MHz respectively, in ppm (δ) using CDCl₃ (downfield from Me₄Si (δ = 0.00)) and CD₃COCD₃ as solvents. Reactions were carried out at a

controlled pH value using a pH-stat apparatus with a combined refillable pH electrode equipped with an Auto Compensating Temperature (ATC) probe. All the epoxides used are known⁸⁻¹⁰ and all thiols employed are commercially available. All β -hydroxysulfides obtained are known compounds⁸⁻¹⁰ except **15** (R = Ts), **16** and those derived from the thiolysis of **7** with butanethiol and from the thiolyses of **9** and **11** with thiophenol that have been herein described as pure compounds.

2-(buthylthio)-1-methylciclohexanol. Obtained as the major regioisomer from the thiolysis of **7** with butanethiol (68% yield); the reaction afforded the two β -hydroxy sulfides regioisomers (α/β = 7/93); by column chromatography on silica gel eluting with 9/1, petroleum ether/diethyl ether of the resulting mixture, there were obtained the major isomer (68% yield) and an enriched mixture of the minor regioisomer (see below, 17% yield). Oil. R_f : 0.22 (1/4- diethyl ether/petroleum ether). IR (CHCl_3): ν = 3519 (m); 2932 (s); 1720 (m); 1465 (s); 1377 (s); 1261 (m); 1131 (m); 1014 (m); 922 (w); 809 (w). ^1H NMR (CDCl_3) δ = 0.90 (*t*, 3H, J = 7.3 Hz), 1.17 (*s*, 3H), 1.23-2.05 (*m*, 12H), 2.52-2.66 (*m*, 3H), 2.76 (*br s*, 1H). ^{13}C NMR (CDCl_3) δ = 13.6; 22.1; 22.4; 23.3; 26.3; 32.3; 32.4; 32.6; 39.5; 58.0; 72.2. GC/MS m/z (%): 202 (100, M^+); 187 (16); 145 (33); 113 (37); 103 (35); 95 (40); 71 (22); 43 (64). Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{OS}$ (202): C, 65.29; H, 10.96; found C, 65.50; H, 11.06.

2-(buthylthio)-2-methylciclohexanol. Obtained as minor regioisomer from the thiolysis of **7** with butanethiol. It has been identified by using an enriched mixture obtained by chromatography on silica gel (9/1 petroleum ether/ diethyl ether) of the resulting reaction mixture. ^1H NMR (CDCl_3) δ = 0.90 (*t*, 3H, J = 7.3 Hz), 1.19 (*s*, 3H), 1.25-2.02 (*m*, 12H), 2.46-2.50 (*m*, 2H), 3.51 (*dd*, 1H, J = 4.3, 10.4 Hz). ^{13}C NMR (CDCl_3) δ = 14.1; 17.9; 22.2; 22.3; 24.4; 25.9; 28.8; 29.7; 31.9; 37.1; 72.5. GC/MS m/z (%): 202 (51, M^+); 143 (12); 113 (73); 95 (100); 83 (14); 69 (22); 55 (24); 43 (21). Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{OS}$ (202): C, 65.29; H, 10.96; found C, 65.15; H, 10.84.

6-(phenylthio)-hexan-1,5-diol. Obtained from the thiolysis of **9** with thiophenol (Table 2 entry 14) and purified by column chromatography on silica gel eluting with diethyl ether (90% yield). Oil. R_f : 0.29 (EtOAc). IR (CHCl_3): ν = 3406 (s); 3007 (m); 2939 (s); 2867 (s); 1719 (w); 1584 (s); 1480 (s); 1439 (s); 1232 (s); 1070 (s); 1025 (s); 917 (m); 825 (w). ^1H NMR 200 MHz (CDCl_3) δ = 1.49-1.59 (m, 6H), 1.99 (br s, 1H), 2.85 (dd, 1H, J = 8.6, 13.6 Hz), 3.13 (dd, 1H, J = 3.7, 13.6 Hz), 3.61-3.71 (m, 3H), 7.23-7.41 (m, 5H). ^{13}C NMR 50.3 MHz (CDCl_3) δ = 21.8; 32.3; 35.6; 42.0; 62.4; 69.2; 126.5; 129.0; 129.9; 135.3. GC/MS m/z : 226 (8, M^+); 135 (6); 124 (100); 109 (13); 85 (19); 57 (8); 45 (8). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}$ (226): C, 63.68; H, 8.02; Found C, 63.82; H, 8.20.

1-(phenylthio)-3-[(trimethylsilyl)oxy]propan-2-ol. Obtained from the thiolysis of **11** with thiophenol (Table 2, entry 18) and purified by re-crystallization with 6/4 diethyl ether/petroleum ether (80% yield). Solid. m. p. : (55-56) °C, (6/4- diethyl ether/petroleum ether). IR (CHCl_3): ν = 3576 (m), 3013 (s), 2959 (m), 1584 (m), 1481 (m), 1439 (m), 1254 (s), 1205 (s), 1091 (s), 845 (s). ^1H NMR 200 MHz (CDCl_3) δ = 0.11 (s, 9H), 2.80 (d, 1H, J = 4.80 Hz), 2.96-3.13 (m, 2H), 3.45-3.66 (m, 2H), 3.69-3.84 (m, 1H), 7.17-7.40 (m, 5H). ^{13}C NMR 50.3 MHz (CDCl_3) δ = -0.7, 36.7, 64.6, 70.0, 126.1, 128.8, 129.2, 135.6. GC/MS m/z : 256 (20, M^+), 149 (9), 129 (100), 123 (50), 73 (67), 45 (17). Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2\text{SSi}$ (256): C, 56.20; H, 7.86; Si, 10.95; Found C, 56.40; H, 7.95; Si, 10.70.

anti-1-(tosyloxy)-3-(phenylthio)-2-hexanol (15) ($\text{R} = \text{Ts}$). Obtained as the major product from the thiolysis of **14** with thiophenol (Table 2, entry 24 and footnote *h*); purified by column chromatography on silica gel eluting with 2/8 diethyl ether/petroleum ether of the resulting three-component mixture. Compound **15** was obtained in 70% yield. Oil. R_f : 0.29 (1/1 diethyl ether/petroleum ether). IR (CHCl_3): ν = 3584 (s); 2962 (s); 2933 (s); 1599 (m); 1584 (m); 1479 (m); 1439 (m); 1360 (s); 1172 (s);

1097 (s). ^1H NMR 200MHz (CDCl_3) δ = 0.89 (t, 3H, J = 6.5 Hz), 1.34-1.77 (m, 4H), 2.44 (s, 3H), 2.58 (br s, 1H), 3.09-3.18 (m, 1H), 3.86 (dd, 1H, J = 5.4, 10.8 Hz), 4.06 (dd, 1H, J = 6.7, 10.1 Hz), 4.22 (dd, 1H, J = 4.2, 10.1 Hz), 7.19-7.39 (m, 7H), 7.73-7.77 (m, 2H). ^{13}C NMR 50.3 MHz (CDCl_3) δ = 13.6; 19.9; 21.3; 31.4, 51.8; 70.6; 71.3; 127.0; 127.6; 128.8; 129.6; 131.7; 132.2; 134.1; 144.8. Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_4\text{S}_2$ (380): C, 59.97; H, 6.36; Found C, 58.95; H, 6.50.

***anti*-1,3-bis(phenylthio)hexan-2-ol (16).** Obtained as minor product from the thiolysis of **14** with thiophenol (Table 2, entry 24 and footnote *h*); purified by column chromatography on silica gel eluting with 2/8, diethyl ether/petroleum ether and isolated in 13% yield. Oil. R_f : 0.45, 1/1 diethyl ether/petroleum ether. IR (CHCl_3): ν = 3530 (m); 3077 (m); 3011 (s); 2962 (s); 2933 (s); 2874 (m); 1583 (m); 1480 (s); 1439 (s); 1276 (m); 1214 (m); 1067 (m); 1025 (s). ^1H NMR 200 MHz (CDCl_3) δ = 0.92 (t, 3H, J = 7.1 Hz), 1.43-1.72 (m, 4H), 2.69 (br s, 1H), 3.04 (dd, 1H, J = 8.2, 13.7 Hz), 3.22 (dd, 1H, J = 4.8, 13.7 Hz), 3.27-3.31 (m, 1H), 3.75-3.80 (m, 1H), 7.19-7.25 (m, 6H), 7.30-7.35 (m, 4H). ^{13}C NMR 50.3 MHz (CDCl_3) δ = 13.9; 20.5; 31.3; 38.4; 54.4; 70.9; 126.6; 127.0; 129.0; 130.0; 131.8; 134.8; 135.1. GC/MS m/z : 318 (82, M^+); 209 (3); 191 (55); 165 (64); 123 (100); 109 (28); 77 (13); 45 (14). Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{OS}_2$ (318): C, 67.88; H, 6.96; Found C, 57.10; H, 7.05.

***anti*-1,2-bis(phenylthio)hexan-3-ol (17).** This compound was isolated in mixture with **16** from the thiolysis of **14** with thiophenol (Table 2, entry 24 and footnote *h*) after silica gel-chromatography.