Convenient Synthesis of Phenyl Sulfides by a Borohydride Exchange Resin-Phenyl Disulfide System in Methanol

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Received December 10, 1993

Since organic sulfur compounds have become increasingly useful and important in organic synthesis,[1,2] convenient preparations of appropriate sulfides, especially those which carry other functional groups, should be important. Although phase-transfer conditions have greatly improved the efficiency of sulfide synthesis from alkyl halides,[3-5] other new synthetic methods have also been developed continuously.[6-12]

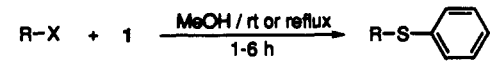
Recently we have found that borohydride exchange resin (BER)[13] readily reduces phenyl disulfide in methanol and the resultant mixture is a convenient and selective reagent for the preparation of phenyl sulfides.[14] Presumably the reagent consists of the mixture of $BH_x(OMe)_y(SPh)_{4-x-y}^-$ attached on the anion-exchange resin (1).[15] In this paper we wish to report the synthesis of phenyl sulfides with 1.

As shown in Table 1,[16] 1 reacts readily with primary bromides and iodides, and somewhat slowly with tosylates, but very sluggishly with chlorides (entries 1-4). This selectivity is quite impressive and not observed previously.[4,8] Secondary bromides reacted slowly. For example, in 6 h at room temperature 2-hexyl bromide gave 2-hexyl phenyl sulfide in 80% yield and cyclohexyl bromide did not react at all; however, at 65 °C 93% yield of 2-hexyl phenyl sulfide and 40% yield of cyclohexyl phenyl sulfide could be obtained (entries 6 and 9). Cyclohexyl phenyl sulfide could be prepared from cyclohexyl iodide (entry 10). Allyl, propagyl, and benzyl halides (including chlorides) reacted readily to give the corresponding sulfides (entries 11-18); however, vinyl halide did not react at all even under reflux (entry 19). Bromochloromethane reacted rapidly but gave 5% of (phenylthio)methyl methyl ether and 45% of bis(phenylthio)methane instead of expected (phenylthio)chloromethane, and bis(phenylthio)-methane was quantitatively obtained using 1.0 equiv of phenyl disulfide (entry 20). However 1-bromo-3-chloropropane and 1-bromo-4-chlorobutane reacted to give 3-chloropropyl phenyl sulfide and 4-chlorobutyl phenyl sulfide quantitatively without affecting Cl (entries 21 and 22). Aromatic halides such as bromobenzene and iodobenzene did not react at all (entry 23). On the other hand α-halo ketones and α-halo acid derivatives reacted readily to afford a convenient synthesis of α-phenylthio ketones and α-phenylthio acid derivatives (entries 24-27).

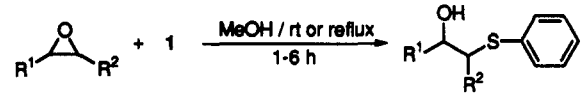
Of the epoxides tested, 1,2-butylene oxide and cyclohexene oxide gave the corresponding β-hydroxy sulfides readily (entries 28 and 29). 1,2-Butylene oxide gave 1-(phenylthio)-2-hydroxybutane exclusively showing the less-hindered site attack of 1; however, styrene oxide gave two products: 2-(phenylthio)-1-phenethyl alcohol and 1-(phenylthio)-2-phenethyl alcohol (1.8:1) (entry 30). Epibromohydrin reacted readily to give 1,3-bis(phenylthio)-2-propanol with 1.0 equiv of phenyl disulfide (entry 32);[17] however, epichlorohydrin gave 1-chloro-3-(phenylthio)-2-propanol (2) quantitatively (entry 31), which was converted to 3-(phenylthio)-1,2-propylene oxide (3) by treating K_2CO_3 (Scheme 2). Since 2 and 3 are not expected to be obtained easily, these will find many applications in organic synthesis.[18] Also we tested the α,β-unsaturated compounds such as 2-cyclohexen-1-one, ethyl crotonate, and crotononitrile (entries 33, 34, and 35). Although benzenethiolate is reported to react with these compounds in 1,4-fashion,[19-21] 1 did not react under the standard conditions.

Finally, in order to find out the selectivity of this system in detail, we carried out the competitive reactions between primary bromide and other functional groups. Octyl bromide reacted selectively with 1 at room temperature in the presence of octyl chloride, octyl tosylate, or 2-hexyl

Scheme 1



R = 1°, 2° alkyl, allyl, propargyl, benzyl, vinyl, aryl, β-carbonyl
X = Cl, Br, I, OTs



R^1 = alkyl, aryl, chloroalkyl R^2 = H, alkyl

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(16) The reaction of octyl bromide is representative. BER (6.06 g, 20 mmol) was added to the methanol solution (100 mL) of phenyl disulfide (1.90 g, 5 mmol) and octyl bromide (1.93 g, 10 mmol), and the mixture was stirred at room temperature for 6 h. Complete reaction was confirmed by GLPC. Then the resin was removed by filtration, and the methanol was evaporated under reduced pressure to give the pure octyl phenyl sulfide (2.13 g, 96%). In the case of α-phenylthio ketones, such as phenacyl bromide, BER was added to the methanol solution of phenyl disulfide and the mixture was stirred under reflux for 1 h to destroy the remaining hydride before the addition of substrate.
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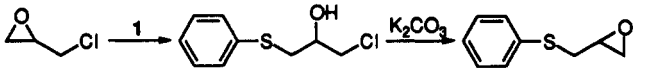
0022-3263/94/1959-3490$04.50/0

Table 1. Synthesis of Phenyl Sulfides by a Borohydride Exchange Resin–Phenyl Disulfide System in Methanol at Room Temperature

entry	substrate	product	yield, % (time, h)
1	octyl chloride	octyl phenyl sulfide	10 (6.0),[b] 28 (1.0)[b,c]
2	octyl bromide	octyl phenyl sulfide	96 (6.0)
3	octyl iodide	octyl phenyl sulfide	96 (3.0)
4	octyl tosylate	octyl phenyl sulfide	97 (3.0)[c]
5	2-hexyl chloride		nr (6.0)[c]
6	2-hexyl bromide	2-hexyl phenyl sulfide	93 (3.0)[c]
7	2-octyl tosylate	2-octyl phenyl sulfide	72 (6.0)[b,c]
8	cyclohexyl chloride		nr (6.0)[c]
9	cyclohexyl bromide	cyclohexyl phenyl sulfide	40 (6.0)[b,c]
10	cyclohexyl iodide	cyclohexyl phenyl sulfide	94 (6.0)[c]
11	allyl chloride	allyl phenyl sulfide	96 (3.0)
12	2-methylallyl chloride	2-methylallyl phenyl sulfide	98 (3.0)
13	allyl bromide	allyl phenyl sulfide	94 (3.0)
14	propagyl bromide	propargyl phenyl sulfide	94 (3.0)
15	benzyl chloride	benzyl phenyl sulfide	95 (3.0)
16	benzyl bromide	benzyl phenyl sulfide	96 (3.0)
17	1-phenethyl bromide	1-phenethyl phenyl sulfide	97 (3.0)
18	*trans*-cinnamyl chloride	*trans*-cinnamyl phenyl sulfide	97 (3.0)
19	2-chloro-1,3-butadiene		nr (3.0)[c]
20	bromochloromethane[d]	bis(phenylthio)methane	96 (3.0)
21	1-bromo-3-chloropropane	3-chloropropyl phenyl sulfide	96 (6.0)
22	1-bromo-4-chlorobutane	4-chlorobutyl phenyl sulfide	96 (6.0)
23	iodobenzene		nr (3.0)[c]
24	ethyl chloroacetate	ethyl (phenylthio)acetate	97 (3.0)
25	ethyl 2-chloropropionate	ethyl 2-(phenylthio)propionate	95 (3.0)
26	phenacyl bromide	2-(phenylthio)acetophenone	95 (1.0)[e]
27	3-chloro-2-butanone	3-(phenylthio)-2-butanone	96 (1.0)[e]
28	1,2-butylene oxide	2-hydroxy-1-(phenylthio)butane	95 (1.0)[c]
29	cyclohexene oxide	*trans*-1-hydroxy-2-(phenylthio)cyclohexane	94 (3.0)[c]
30	styrene oxide	2-(phenylthio)-1-phenethyl alcohol	66 (3.0)[b]
		1-(phenylthio)-2-phenethyl alcohol	33
31	epichlorohydrin	1-chloro-3-(phenylthio)-2-propanol	95 (3.0)
32	epibromohydrin[d]	1,3-bis(phenylthio)-2-propanol	95 (3.0)
33	2-cyclohexen-1-one		nr (3.0)[c,e]
34	ethyl crotonate		nr (3.0)[c]
35	crotonitrile		nr (3.0)[c]

[a] Isolated yields. [b] Yields determined by GLPC. [c] Reflux. [d] Reaction with 1.0 equiv of disulfide. [e] Before the addition of substrate, phenyl disulfide was reacted with BER and refluxed for 1.0 h to destroy the remaining hydride.

Scheme 2



2 3

bromide. Reaction of 1,2-butylene oxide was slower than octyl bromide and showed only moderate selectivity (0.4:1). On the other hand, reaction of octyl iodide was faster than octyl bromide with moderate selectivity (3:1) at 0 °C. Reactive halides, such as benzyl bromide and ethyl bromoacetate, reacted selectively with 1 at 0 °C in the presence of octyl bromide.

Beside the essentially quantitative formation of phenyl sulfides using a stoichiometric amount of phenyl disulfide under neutral conditions[22] and the unique selectivity, the BER–phenyl disulfide system has another significant advantage over other systems.[4-6] Simple separation of resin by filtration gives the methanol solution of products essentially free from the sulfur and boron moiety.

Experimental Section

General. $NaBH_4$ (98% Nisso Ventron) was used without further purification. Anion-exchange resin (Amberite IRA-400) was used supporting the polymer of BER. All of the organic materials were obtained from commercial suppliers and were used without further purification. Commercial grade 99.5% methanol was used as solvent. The ^1H NMR spectra were obtained with tetramethylsilane as an internal standard.

Preparation of the Borohydride Exchange Resin. An aqueous solution of sodium borohydride (1 M, 1 L) was stirred with wet chloride-form anion-exchange resin (Amberlite IRA-400 [20–50 mesh], 200 g) for 1 h at room temperature. The resulting resin was washed thoroughly with distilled water until free from excess $NaBH_4$. The borohydride form anion-exchange resin was then dried *in vacuo* at 60 °C for 5 h. The dried resin was analyzed for borohydride content by hydrogen evolution on acidification with 2 N HCl and the average hydride content of BER was found to be 3.3 mmol of BH_4^- per gram. The dried resin was stored under nitrogen in a refrigerator (~4 °C). The hydride content was constant over 6 weeks.

General Procedure for the Preparation of Phenyl Sulfides. The reaction of octyl bromide is representative. BER (6.06 g, 20.0 mmol) was added to the methanol solution (100 mL) of octyl bromide (1.93 g, 10.0 mmol) and phenyl disulfide (1.09 g, 5.0 mmol), and the mixture was stirred at room temperature for 6 h. Complete reaction was confirmed by GLPC. Then the resin was removed by filtration and the methanol was evaporated under reduced pressure to give the pure octyl phenyl sulfide (2.13 g, 96%): n^{22}_D 1.5243 (lit.[23] n^{22}_D 1.5247); ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H, J = 7.0), δ 1.30 (s, 8 H), δ 1.46 (m, 2 H), δ 1.68 (m, 2 H), δ 2.95 (t, 2 H, J = 7.0), δ 7.15–7.38 (m, 5 H); IR (neat) 3075, 2955, 2926, 2854, 1586, 1478, 1439, 1090, 1026 cm^{-1}; GCMS m/z (relative intensity) (EI, 70 eV) 222 (M^+ 25), 123 (20), 110 (100), 109 (10), 43 (18), 41 (19).

2-Hexyl phenyl sulfide: ^1H NMR ($CDCl_3$) δ 0.94 (t, 3 H, J = 6.9), δ 1.26–1.74 (m, 9 H), δ 3.24 (q, 1 H, J = 6.9), δ 7.29 (m, 3 H), δ 7.42 (m, 2 H); IR (neat) 3073, 2959, 2930, 2872, 1586, 1478, 1437, 1090, 1026 cm^{-1}; GCMS m/z (relative intensity) (EI, 70 eV)

(22) Excess NaOH was used for the preparation of sulfide with thiophenol and phase-transfer catalysts. See ref 4–6.

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194 (M^+ 21), 110 (100), 109 (14), 43 (44), 41 (16). Anal. Calcd for $C_{12}H_{18}S$: C, 74.74; H, 9.67; S, 15.39. Found: C, 74.99; H, 9.54; S, 15.47.

Cyclohexyl phenyl sulfide: n^{22}_D 1.5654 (lit.[24] n^{22}_D 1.5656); ^{1}H NMR ($CDCl_3$) δ 1.20–1.49 (m, 5 H), δ 1.64 (m, 1 H), δ 1.80 (m, 2 H), δ 2.01 (m, 2 H), δ 3.11 (m, 1 H), δ 7.18–7.35 (m, 3 H), δ 7.37–7.42 (m, 2 H); IR (neat) 3073, 2930, 2853, 2584, 1479, 1439, 1090, 1026 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 192 (M^+ 23), 110 (100), 109 (20), 55 (33), 41 (16).

Allyl phenyl sulfide: n^{22}_D 1.5764 (lit.[25] n^{22}_D 1.5755); ^{1}H NMR ($CDCl_3$) δ 3.58 (m, 2 H), δ 5.05–5.21 (m, 2 H), δ 5.83–5.98 (m, 1 H) δ 7.18–7.41 (m, 5 H); IR (neat) 3077, 2974, 2914, 1649, 1586, 1479, 1439, 1090, 1011, 897 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 150 (M^+ 93), 149 (23), 135 (85), 117 (75), 115 (31), 110 (25), 109 (73), 91 (26), 65 (36), 51 (25), 45 (27), 41 (100).

2-Methylallyl phenyl sulfide: n^{22}_D 1.5778 (lit.[26] n^{25}_D 1.5782); ^{1}H NMR ($CDCl_3$) δ 1.90 (s, 3 H), δ 3.56 (s, 2 H), δ 4.85 (s, 2 H), δ 7.17–7.39 (m, 5 H); IR (neat) 3077, 2974, 2914, 1649, 1586, 1479, 1439, 1090, 1012, 897 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 164 (M^+ 78), 149 (37), 131 (28), 110 (33), 109 (25), 91 (26), 77 (14), 65 (24), 55 (100).

Propagyl phenyl sulfide: n^{22}_D 1.6001 (lit.[27] n^{20}_D 1.6006); ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 1 H), δ 3.63 (s, 2 H), δ 7.30 (m, 3 H), δ 7.46 (m, 2 H); IR (neat) 3291, 3059, 2949, 2917, 1672, 1586, 1481, 1439, 1088, 1026 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 148 (M^+ 26), 147 (100), 115 (10), 110 (3), 109 (26), 65 (13).

Benzyl phenyl sulfide: mp 40–41 °C (lit.[28] mp 40–41 °C); ^{1}H NMR ($CDCl_3$) δ 4.14 (s, 2 H), δ 7.15–7.35 (m, 10 H); IR (neat) 3061, 3028, 2971, 2924, 1583, 1479, 1439, 1026 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 200 (M^+ 16), 109 (6), 91 (100), 65 (17).

1-Phenethyl phenyl sulfide: ^{1}H NMR ($CDCl_3$) δ 1.65 (d, 3 H, J = 7.2), δ 4.25 (q, 1 H, J = 7.2), δ 7.15–7.35 (m, 10 H); IR (neat) 3061, 3028, 2971, 2924, 1583, 1479, 1439, 1089, 1026 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 214 (M^+ 16), 110 (19), 109 (16), 106 (17), 105 (100), 103 (16), 79 (14), 77 (22). Anal. Calcd for $C_{14}H_{14}S$: C, 78.46; H, 6.58; S, 14.96. Found: C, 78.35; H, 6.68; S, 14.97.

***trans*-Cinnamyl phenyl sulfide**: mp 77–78 °C (lit.[29] 78–78.5 °C); ^{1}H NMR ($CDCl_3$) δ 3.72 (d, 2 H, J = 7.1), δ 6.38 (dt, 1 H, J = 15.0, 7.1), δ 6.44 (d, 1 H, J = 15.0), δ 7.14–7.40 (m, 10 H); IR (neat) 3077, 3032, 2912, 1579, 1479, 1435, 1090, 963 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 226 (M^+ 4), 118 (11), 117 (100), 115 (39), 109 (8), 91 (12).

Bis(phenylthio)methane: ^{1}H NMR ($CDCl_3$) δ 4.40 (s, 2 H), δ 7.32 (m, 6 H), δ 7.48 (m, 4 H); IR (neat) 3059, 2920, 1584, 1479, 1439, 1200, 1088, 1027 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 232 (M^+ 13), 123 (100), 109 (12), 77 (22), 65 (12), 51 (19), 45 (39). Anal. Calcd for $C_{13}H_{12}S_2$: C, 67.20; H, 5.21; S, 27.60. Found: C, 67.11; H, 5.41; S, 27.48.

3-Chloropropyl phenyl sulfide: n^{22}_D 1.5749 (lit.[30] n^{20}_D 1.5752); ^{1}H NMR ($CDCl_3$) δ 2.08 (tt, 2 H, J = 6.8, 7.0), δ 3.09 (t, 2 H, J = 7.0), δ 3.67 (t, 2 H, J = 6.8), δ 7.17–7.41 (m, 5 H); IR (neat) 3075, 2959, 2926, 1584, 1481, 1439, 1267, 1090, 1026 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 188 (M+2 27), 186 (M^+ 66), 123 (100), 110 (84), 109 (29), 77 (19), 65 (21), 45 (23).

4-Chlorobutyl phenyl sulfide: n^{22}_D 1.5681 (lit.[30] n^{20}_D 1.5678); ^{1}H NMR ($CDCl_3$) δ 1.81 (m, 2 H), δ 1.93 (m, 2 H), δ 2.95 (t, 2 H, J = 6.9), δ 3.56 (t, 2 H, J = 6.9), δ 7.15–7.38 (m, 5 H); IR (neat) 3076, 2959, 2926, 1584, 1481, 1439, 1268, 1090, 1026 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 202 (M + 2, 15), 200 (40), 123 (100), 110 (77), 109 (22), 91 (32), 77 (14), 65 (16), 55 (37), 45 (24).

Ethyl (phenylthio)acetate: ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3 H, J = 7.1), δ 3.63 (s, 2 H), δ 4.17 (q, 2 H, J = 7.1), δ 7.26 (m, 3 H), δ 7.40 (m, 2 H); IR (neat) 3061, 2984, 1736, 1583, 1481, 1439, 1277, 1134, 1026 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 196 (M^+ 48), 123 (100), 110 (5), 109 (13), 77 (13), 45 (30). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16; S, 16.34. Found: C, 61.08; H, 6.28; S, 16.38.

Ethyl 2-(phenylthio)propionate: ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 3 H, J = 7.1), δ 1.52 (d, 3 H, J = 7.3), δ 4.82 (q, 1 H, J = 7.3), δ 4.15 (q, 2 H, J = 7.1), δ 7.30 (m, 3 H), δ 7.49 (m, 2 H); IR (neat) 3061, 2985, 1736, 1584, 1481, 1439, 1278, 1134, 1026 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 210 (M^+ 22), 137 (100), 135 (14), 110 (7), 109 (27). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.76; H, 6.98; S, 15.17.

2-Hydroxy-1-(phenylthio)butane: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3 H, J = 7.4), δ 1.57 (m, 2 H), δ 2.47 (br s, 1 H), δ 2.86 (dd, 1 H, J = 8.4, 13.4), δ 3.13 (dd, 1 H, J = 3.6, 13.4), δ 3.61 (m, 1 H), δ 7.18–7.41 (m, 5 H); IR (neat) 3550–3100, 3074, 2964, 2926, 2878, 1583, 1479, 1439, 1232, 1089, 1024, 972 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 182 (M^+ 26), 124 (100), 123 (21), 110 (19), 109 (21), 91 (24), 78 (16), 59 (15), 45 (16). Anal. Calcd for $C_{10}H_{14}OS$: C, 65.89; H, 7.74; S, 17.59. Found: C, 65.82; H, 7.94; S, 17.39.

***trans*-1-Hydroxy-2-(phenylthio)cyclohexane**: n^{22}_D 1.5822 (lit.[31] n^{25}_D 1.5825); ^{1}H NMR ($CDCl_3$ + D_2O) δ 1.19–1.41 (m, 4 H), δ 1.70 (m, 2 H), δ 2.11 (m, 2 H), δ 2.78 (m, 1 H), δ 3.34 (m, 1 H), δ 7.29 (m, 3 H), δ 7.47 (m, 2 H); IR (neat) 3550–3100, 3057, 2934, 2859, 1583, 1476, 1438, 1356, 1269, 1066, 1037, 926 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 208 (M^+ 17), 110 (100), 109 (15), 98 (10), 81 (27), 65 (12).

1-Chloro-3-(phenylthio)-2-propanol (2): ^{1}H NMR ($CDCl_3$) δ 2.72 (br s, 1 H), δ 3.12–3.24 (m, 2 H), δ 3.68 (d, 2 H, J = 4.8), δ 3.88–4.00 (m, 1 H), δ 7.19–7.44 (m, 5 H); IR (neat) 3550–3100, 3059, 2955, 2924, 1583, 1481, 1438, 1298, 1043 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 204 (M + 2, 9), 202 (M^+ 25), 158 (13), 123 (100), 110 (17), 109 (17), 77 (14), 65 (10), 45 (35). Anal. Calcd for $C_9H_{11}ClOS$: C, 53.33; H, 5.47; S, 15.82. Found: C, 53.47; H, 5.68; S, 15.80.

1,3-Bis(phenylthio)-2-propanol: ^{1}H NMR ($CDCl_3$) δ 2.40 (br s, 1 H), δ 3.07 (dd, 2 H, J = 7.0, 13.7), δ 3.21 (dd, 2 H, J = 4.9, 13.7), δ 4.85 (m, 1 H), δ 7.26–7.40 (m, 10 H); IR (neat) 3550–3100, 3057, 2920, 2583, 1479, 1436, 1419, 1273, 1085, 1024 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 276 (M^+ 33), 149 (96), 135 (77), 124 (100), 123 (78), 110 (33), 109 (48), 91 (20), 77 (29), 45 (61). Anal. Calcd for $C_{15}H_{16}OS_2$: C, 65.18; H, 5.83; S, 23.20. Found: C, 65.06; H, 6.05; S, 22.98.

Preparation of 3-(Phenylthio)-1,2-propylene Oxide (3). BER (6.06 g, 20.0 mmol) was added to the methanol solution (100 mL) of epichlorohydrin (0.92 g, 10.0 mmol) and phenyl disulfide (1.09 g, 5.0 mmol), and the mixture was stirred at room temperature for 3 h to complete the preparation of 1-chloro-3-(phenylthio)-2-propanol. K_2CO_3 (4.14 g, 30 mmol) solution in water (10 mL) was added to the reaction flask and the mixture was stirred at room temperature for 3 h. Then the resin was removed by filtration. The methanol solution was diluted with saturated NaCl solution (50 mL) and extracted with methylene chloride (3 × 50 mL). The methylene chloride layer was dried over $MgSO_4$ and evaporated under reduced pressure to give the pure 3-(phenylthio)-1,2-propylene oxide (1.54 g, 93%): ^{1}H NMR ($CDCl_3$) δ 2.51 (m, 1 H), δ 2.76 (m, 1 H), δ 2.94 (m, 1 H), δ 3.17 (m, 2 H), δ 7.28 (m, 3 H), δ 7.43 (m, 2 H); IR (neat) 3057, 2993, 2920, 1586, 1481, 1436, 1263, 1088 cm^{-1}; GCMS *m/z* (relative intensity) (EI, 70 eV) 166 (M^+, 8), 123 (14), 110 (77), 109 (34), 77 (35), 69 (33), 66 (44), 65 (69), 57 (25), 51 (69), 45 (100). Anal. Calcd for $C_9H_{10}OS$: C, 65.03; H, 6.06; S, 19.29. Found: C, 65.23; H, 6.25; S, 19.27.

General Procedure for the Preparation of α-Phenylthio Ketones. The reaction of phenacyl bromide is representative. BER (6.06 g, 20.0 mmol) was added to the methanol solution (100 mL) of phenyl disulfide (1.09 g, 5.0 mmol) solution in methanol (100 mL), and the mixture was stirred under reflux for 1 h to complete reduction of phenyl disulfide and destroy the remaining hydride. Then the solution was cooled to room temperature and phenacyl bromide (1.99 g, 10.0 mmol) was added to the reaction flask. The mixture was stirred at room tem-

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perature for 1 h to complete reaction. Complete reaction was confirmed by GLPC. Then the resin was removed by filtration and the methanol was evaporated under reduced pressure to give the pure 2-(phenylthio)acetophenone (2.17 g, 95%): ^{1}H NMR ($CDCl_3$) δ 4.29 (s, 2 H), δ 7.21–7.61 (m, 8 H), δ 7.97 (m, 2 H); IR (neat) 3059, 2936, 1680, 1597, 1580, 1481, 1449, 1477, 1200, 1024 cm^{-1}; GCMS m/z (relative intensity) (EI, 70 eV) 228 (M^+ 18), 110 (2), 109 (5), 105 (100), 77 (29). Anal. Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 7.01; S, 14.84. Found: 73.61; H, 7.11; S, 14.80.

3-(Phenylthio)-2-butanone: n^{22}_D 1.5558 (lit.[32] n^{20}_D 1.5563); ^{1}H NMR ($CDCl_3$) δ 1.40 (d, 3 H, J = 7.3), δ 2.30 (s, 3 H), δ 3.77 (q, 1 H, J = 7.3), δ 7.21–7.42 (m, 5 H); IR (neat) 3075, 2976, 2930, 1711, 1583, 1479, 1438, 1354, 1228, 1159, 1064, 1024 cm^{-1}; GCMS m/z (relative intensity) (EI, 70 eV) 180 (M^+ 25), 137 (100), 135 (20), 110 (6), 109 (35).

Competitive Reaction of Octyl Bromide in the Presence of Other Alkyl Halides, Tosylates, or Epoxides. The competitive reaction between octyl bromide and octyl chloride is representative. BER (2.0 mmol) was added to the reaction flask containing octyl bromide (1.0 mmol), octyl chloride (1.0 mmol), and phenyl disulfide (0.5 mmol) solution in methanol (10 mL), and the mixture was stirred at room temperature. After 6.0 h, GLPC analysis showed 100% octyl phenyl sulfide resulting from the reaction of octyl bromide and no reaction of octyl chloride.

Acknowledgment. This work was supported by the Organic Chemistry Research Center sponsored by the Korea Science and Engineering Foundation.

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