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THE PREPARATION OF β-HYDROXYSULFOXIDES

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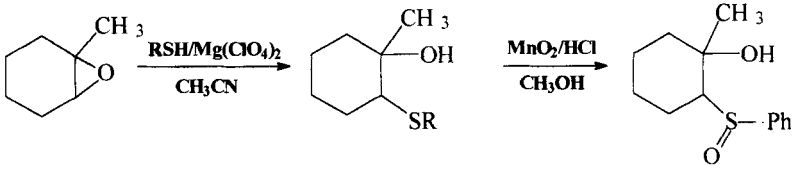
Abstract. Oxidation of β-hydroxy thioethers with MnO_2-aqu.35%/HCl in methanol gives β-hydroxy sulfoxides in high yields.

β-Hydroxy sulfoxides[1] are used in the synthesis of natural substrates[2] and are intermediates in many organic reactions[3].

Recently we reported an high yields procedure for alkyl sulfoxides preparation



Scheme 1

by treating alkyl sulfides with 5% molar excess of MnO_2-TMCS or MnO_2-HCl (1:3 in CH_3OH)[4]. This latter reagent has now been applied to the oxidation of β-hydroxy sulfides.

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The substrate have been prepared according to M.Chini[6] by oxirane ring cleavage with thiols in anhydrous acetonitrile; better yields have been obtained by replacing $LiClO_4$ with $Mg(ClO_4)_2$.

The yields of the oxidation reaction are very stisfactory **(Table 1)**. In no case, even from tertiary alcohols, substitution by chlorine anion has been observed.

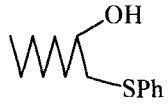
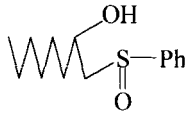
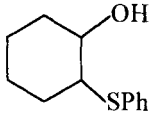
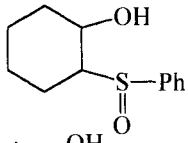
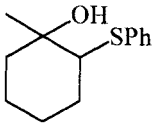
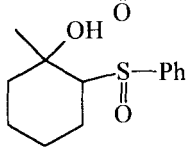
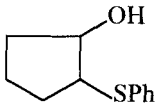
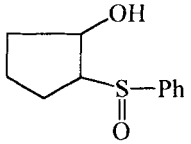
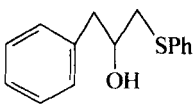
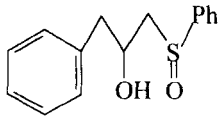
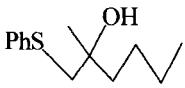
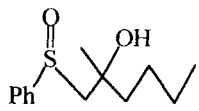
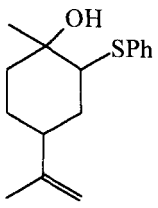
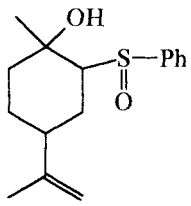
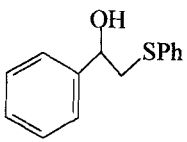
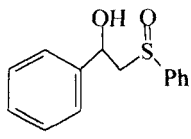
The process likely occurs through a sulphur radical cation, already suggested[7] for monoalkyl sulphides oxidation by MnO_2/HCl.

Experimental

Starting Materials. Not commercially available oxiranes (1-3-6) were prepared from the corresponding olefines[5].

General reaction procedure. MnO_2 (Merck, 90%, activated, precipitated) (21 mmoles) was added to a stirred solution of sulfide (20 mmoles) in CH_3OH (10 ml) in a two necked-round bottomed flask (50 ml), equipped with a dropping funnel and a thermometer. The mixture was cooled to 0°C in an ice bath and aqueous 35% HCl (63 mmoles) slowly dropped, internal temperature not exceeding 10°C. The solution was stirred and the reaction progress monitored by TLC (n.pentane/diethyl ether 1:1). After the time reported in **Table 1**, the solution was poured in brine (70 ml), neutralised with 1M NaOH and extracted with CH_2Cl_2 (4 x 20 ml). The organic phases were collected, dried over (Na_2SO_4) and evaporated. The residue was chromatographed on silica gel by a n.pentane/diethyl ether gradient. The yields were calculated on products isolated by preparative TLC. Yields of low boiling sulfoxides were calculated by capillary GC (Chromopac CP-Wax 52 CD column) with decane as internal standard.

Table

Item	Sulfide (a)	Yield (%)	Reaction time(h)	Sulfoxide (b)	Yield (%)	Reaction time(h)
1		90	18		83	18
2		87	17		81	6
3		88	20		80	18
4		91	21		78	22
5		89	18		83	13
6		83	42		84	25
7		88	27		82	19
8		94	18		94	8

1-phenylthio-2-Octanol (1a): ^{1}H-NMR δ 0.86 (3H,t, CH3); 1.04-1.65 (10H, br.s., $(CH_2)_5$); 2.82 (2H, m, CH_2-S); 3.66 (1H, br.s., CH-OH); 7.34 (5H, Ar). Anal. Calcd. for $C_{14}H_{22}OS$ C, 70.54; H, 9.30; S, 13.45. Found C, 70.35; H, 9.55; S, 13.31.

1-phenylsulfinyl-2-Octanol (1b): ^{1}H-NMR δ 0.89 (3H, t, CH3); 1.04-1.65 (10H, br.s., $(CH_2)_5$); 3.88 (2H, d, J=6.05 Hz); 4.13-4.43 (1H, br.s., CH-OH) 765 (5H, Ar.).**(2b):** Yield 63 % m.p. 130-31; ^{1}H-NMR δ 1.08-1.54 (4H, m, $(CH_2)_2$); 1.7-2.04 (4H, m, $(CH_2)_2$); 3.14 (2H, m, CH-O-CH). Anal. Calcd. for $C_{14}H_{22}O_2S$ C, 66.10; H, 8.72; S, 12.60. Found C, 66.18; H, 8.55; S, 12.68.

2-Phenylthiocyclohexan-1-ol (2a): IR 3338 cm^{-1}; ^{1}H-NMR δ ($CDCl_3$) 1.34-2.43 (m, 8H), 2.89 (m, 1H), 3.46 (m,1H). Anal. Calcd. for $C_{12}H_{16}OS$ C, 69.19; H, 7.74; S, 15.39. Found C, 69.00; H, 7.90; S, 15.50

2-phenylsulfinyl-1-cyclohexanol (2b): Ir and NMR as reported G.H. Posner, and D.Z. Rogers, J.Am.Chem. Soc. 1977, 99, 8208. Anal. Calcd. for $C_{12}H_{16}O_2S$ C, 64.25; H, 7.19; S, 14,29. Found C, 64.12; H, 7.31; S, 14,14.

1-methyl-2-phenylthio-1-cyclohexanol (3a): ^{1}H-NMR δ 0.91–1.42 (6H, br.s., $(CH_2)_3$); 1.21 (3H, t,CH_3); 3.31-3.62 (3H, m); 7.22 (5H, Ar). Anal. Calcd. for $C_{13}H_{18}OS$ C, 70.23; H, 8.16; S, 14.42. Found C, 70.11; H, 8.33; S, 14.28

1-methyl-2-phenysulfinyl-1-cyclohexanol (3b): m.p.129-134°C; IR(nujol) 3461, 1013 cm^{-1}, ^{1}H-NMR δ 0.93-1.88 (6H, br.s., $(CH_2)_3$); 1.22 (3H, t, CH_3); 3.28 (2H, m, CH_2); 3.72 (1H, m, CH-S); 7.11-7.62 (5H, Ar). Anal. Calcd. for $C_{13}H_{18}O_2S$ C, 65.51; H, 7.61; S, 13.45. Found C, 65.33; H, 7.77; S, 13.55.

2-phenylthio-1-cyclopentanol (4a): ^{1}H-NMR δ 1.31-2.42 (6H,m, $(CH_2)_3$); 3.89-4.09 (1H, m, CH-S); 4.10-4.31 (1H, m, CH-O); 7.13-8.06 (5H, Ar). Anal. Calcd. for $C_{11}H_{14}OS$ C, 68.00; H, 7.26; S, 16.50. Found C, 68.07; H, 7.20; S, 16.43.

2-phenylsulfinyl-1-cyclopentanol (4b): ^{1}H-NMR δ 1.17-2.06 (6H, m, $(CH_2)_3$); 3.41-3.72 (1H, m, CH-S); 4.02 (1H, m, CH-O); 7.17-8.04 (5H, Ar).$C_{11}H_{14}O_2S$ C, 62.83; H, 6.71; S, 15.25. Found C, 62.77; H, 6.80; S, 15.31.

3-phenyl-1-phenylthiopropan-2-ol (5a): ^{1}H-NMR δ 2.74-2.92 (2H, m, CH_2); 3.12-3.42 (2H, m, CH_2); 3.72-4.10 (1H, m, CH); 7.16 (10H, Ar.). Anal. Calcd. for $C_{15}H_{16}OS$ C, 73.73; H, 6.60; S, 13.12. Found C, 73.60; H, 6.90; S, 13.01.

3-phenyl-1-phenylsulfinylpropan-2-ol (5b): ^{1}H-NMR δ 2.68-3.19 (4H, m, 2(CH_2); 4.48 (1H, m, CH); 7.04-7.68 (10H, Ar). Anal. Calcd. for $C_{15}H_{16}O_2S$ C, 69.20; H, 6.19; S, 12.31. Found C, 69.07; H, 6.27; S, 12.18.

2-methyl-1-phenylthiohexan-2-ol (6a): ^{1}H-NMR δ 0.82 (3H, m, CH_3); 0.9-1.48 (6H, br.s., $(CH_2)_3$); 1.12 (3H, s, CH_3); 3.42 (2H, s, CH_2-S); 6.93-7.58 (5H, Ar). Anal. Calcd. for $C_{13}H_{20}O_2S$ C, 69.59; H, 8.98; S, 14.29. Found C, 69.57; H, 8.99; S, 14.23.

2-methyl-1-phenylsulfinylhexan-2-ol (6b): ^{1}H-NMR δ 0.86 (3H, t, CH_3); 1.12-1.54 (6H, m, $(CH_2)_3$); 1.30 (3H, s, CH_3); 3.63 (2H, s, CH_2); 7.13-7.78 (5H, Ar). Anal. Calcd. for $C_{13}H_{20}O_2S$ C, 64.96; H, 8.39; S, 13.34. Found C, 64.91; H, 8.47; S, 13.38.

1-methyl-4-(1-methyl-1-ethenyl)-2-phenylsulfinyl-1-cyclohexanol (7a): ^{1}H-NMR δ 0.87-2.48 (7H, br.s.); 1.21 (3H, s, CH3); 1.72 (3H, s, CH3); 2.97 (1H, m CH); 4.70 (2H, m, CH2=); 7.03-7.62 (5H, Ar). Anal. Calcd. for $C_{16}H_{22}OS$ C, 73.23; H, 8.45; S, 12.22. Found C, 73.18; H, 8.51; S, 12.15.

1-methyl-4-(1-methyl-1-ethenyl)-2-phenylthio-1-cyclohexanol (7b): ^{1}H-NMR δ 0.89-2.32 (7H, br.s.); 1.28 (3H, s, CH_3); 1.69 (3H, s, CH_3); 3.33 (1H, t, J= 6.4Hz, CH); 4.72 (2H, m, CH_2); 7.04- 7.60 (5H, Ar). Anal. Calcd. for $C_{16}H_{22}O_2S$ C, 69.03; H, 7.96; S, 11.52. Found C, 69.09; H, 7.91; S, 11.48.

1-phenyl-2-phenylthioethan-1-ol (8a): ^{1}H-NMR δ 3.81 (2H, d, J=6.58Hz, CH_2); 4.27 (1H, t, J=6.58Hz, CH); 7.10 (10H, Ar). Anal. Calcd. for $C_{15}H_{18}OS$ C, 73.13; H, 7.36; S, 13.01. Found C, 73.00; H, 7.58; S, 13.09

1-phenyl-2-phenylsulfinylethan-1-ol (8b): ^{1}H-NMR δ 3.93 (2H, d, J=6.58Hz, CH_2); 4.42 (1H, t, J=6.58Hz, CH); 6.88-7.41 (10H, Ar). Anal. Calcd. for $C_{15}H_{18}O_2S$ C, 68.67; H, 6.92; S, 12.22. Found C, 68.60; H, 6.99; S, 12.14.

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