A Facile Synthesis of (*R*)-1-Benzyloxy-3-buten-2-ol

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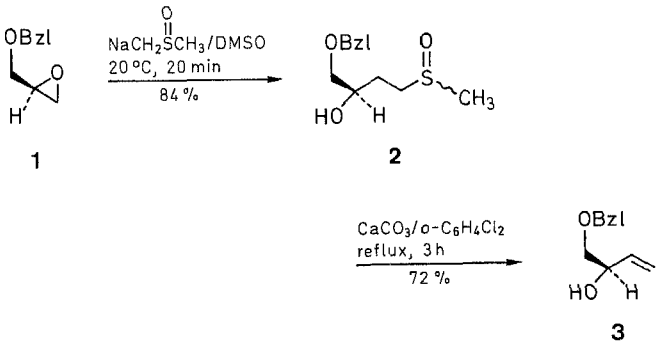
A functionalized optically active allyl alcohol, (*R*)-1-benzyloxy-3-buten-2-ol, is efficiently prepared from (*S*)-*O*-benzylglycidol in two steps.

Molecules possessing a chiral allyl alcohol moiety are useful starting materials for the construction of a variety of optically active compounds as they can serve as substrates for various chemical conversions such as sigmatropic reactions.[1] We report here a facile two-step preparation of (*R*)-1-benzyloxy-3-buten-2-ol (**3**),[2] a potentially useful functionalized chiral allyl alcohol, using (*S*)-*O*-benzylglycidol (**1**).[3] Stirring a solution of (*S*)-2-(benzyloxymethyl)oxirane [(*S*)-*O*-benzylglycidol] (**1**) in dimethyl sulfoxide containing two equivalents of sodium methylsulfinylmethide[4] generated *in situ* in the same reaction medium affords (*R*)-4-benzyloxy-3-hydroxybutyl methyl sulfoxide (**2**) in 84% yield after 20 min. Although thermolysis of



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the sulfoxide **2** with calcium carbonate in boiling toluene[5] is found to proceed very sluggishly to give the desired (*R*)-1-benzyloxy-3-buten-2-ol **(3)**, the reaction occurs in more facile and cleaner manner to furnish **3** in 73% yield after 3 h when boiling *o*-dichlorobenzene is used as solvent in place of boiling toluene. The enantiomeric (*S*)-1-benzyloxy-3-buten-2-ol **(3)** may also be obtained by employing the same sequence starting from (*R*)-*O*-benzylglycidol **(1)**, which is readily accessible.[6]

Optical rotations were measured with a JASCO-DIP-4 automatic polarimeter. Mass spectra were recorded with a JEOL-OISG-2 instrument, IR spectra with a JASCO A-102 spectrophotometer, and ^{1}H-NMR spectra on JEOL-JNM-FX90A (90 MHz) and JEOL-JNM-GX500 (500 MHz) spectrometers.

Reactions were carried out under argon.

(*R*)-4-Benzyloxy-3-hydroxybutyl Methyl Sulfoxide (2):

NaH (washed with hexane; 2.68 g, 67.1 mmol) is added portionwise to DMSO (50 mL) at 0 °C with stirring, the solution is warmed to 60 °C for 70 min, then cooled to room temperature. (*S*)-2-(Benzyloxymethyl)oxirane (**1**; 5.0 g, 30.5 mmol) in DMSO (10 mL) is added dropwise to the stirred solution and stirring is continued for 20 min at room temperature. The mixture is diluted with 5% aqueous $NaHCO_3$ (30 mL), then extracted with CH_2Cl_2 (3 × 50 mL). The wet CH_2Cl_2 extract is evaporated by water pump followed by rotary pump (< 60 °C) to remove most of the solvents. The oily residue is chromatographed on a silica gel column (90 g) using Et_2O as eluent to give **2** as a pale yellow oil; yield: 6.2 g (84%).

$C_{12}H_{18}O_3S$	calc.	C 59.48	H 7.49	S 13.23
(242.2)	found	59.32	7.60	13.59

MS (70 eV): m/z = 242 (M^+), 170, 91 (100%).

IR (neat): ν = 3400 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.78–2.30 (m, 2H); 2.58 (s, 3H); 3.32–3.63 (m, 2H); 2.70–3.20 (m, 3H, ^{1}H exchangeable); 3.76–4.15 (m, 1H); 4.56 (s, 2H); 7.33 (s, 5H).

(*R*)-1-Benzyloxy-3-buten-2-ol (3):

In a solution of the sulfoxide **2** (3.63 g, 15 mmol) in *o*-dichlorobenzene (55 mL), $CaCO_3$ (4.5 g, 45 mmol) is suspended and this suspension is refluxed for 3 h with stirring. After cooling, the mixture is filtered through Celite and the filtrate is directly chromatographed on a silica gel column (100 g) using hexane/Et_2O (1:1) as eluent to give **3** as a colorless oil; yield: 1.94 g (72.7%); bp 95–100 °C/0.5 Torr (Kugelrohr); $[\alpha]_D^{24}$ + 4.72° (c = 1.10, $CHCl_3$) [100% e.e. by ^{1}H-NMR (500 MHz) of the MTPA ester] (Lit. $[\alpha]_D$ + 5.3° (c = 0.37, $CHCl_3$);[2b] $[\alpha]_D$ + 6.2°, (c = 1.6, $CHCl_3$).[2c]

$C_{11}H_{14}O_2$	calc.	C 74.13	H 7.92
(178.2)	found	74.40	7.72

MS (70 eV): m/z = 178 (M^+), 160, 91 (100%).

IR (neat): ν = 3450 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 2.39 (s, 1H exchangeable); 3.26–3.63 (m, 2H); 4.57 (s, 2H); 4.24–4.44 (m, 1H); 5.11–6.04 (m, 3H); 7.33 (s, 5H).

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(1) For example, see: Hill, R.K., in: *Asymmetric Synthesis*, Morrison, J.D. (ed.), Vol. 3, Academic Press, New York, 1984, p. 503.
(2) Recently, three alternative syntheses of (*R*)-1-benzyloxy-3-buten-2-ol **(3)** were reported.
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(4) Corey, E.J., Chaykovsky, M. *J. Am. Chem. Soc.* **1962**, *84*, 866.
(5) Trost, B.M., Saltzman, T.N. *J. Am. Chem. Soc.* **1973**, *95*, 6840.
(6) Takano, S., Seya, K., Goto, E., Hirama, M., Ogasawara, K. *Synthesis* **1983**, 116.