Lipase-Mediated Preparation of Optically Pure Four-Carbon Di- and Triols from a *meso*-Precursor

Osamu Yamada, Kunio Ogasawara*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980-77, Japan
Fax +81(22)2176845; E-mail c21799@cctu.cc.tohoku.ac.jp
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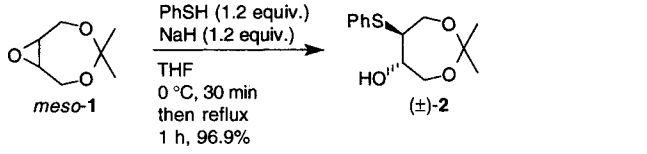
An expedient route to optically pure four-carbon di- and triols, prepared from a *meso*-symmetric four-carbon precursor by employing lipase-mediated kinetic resolution as a key step.

Optically active four-carbon polyols are extremely useful for the construction of a wide variety of optically active materials as chiral building blocks. Most of them are conveniently obtained[1,2] from naturally occurring four-carbon precursors, such as malic and tartaric acid, which are available in both enantiomeric forms. We wish to report here a new lipase-mediated procedure for the preparation of some chiral four-carbon polyols potentially useful as chiral building blocks starting from a *meso*-symmetric four-carbon epoxide[3] readily accessible from *cis*-2-butene-1,4-diol.

The *meso*-epoxide[3] **1**, prepared in two steps in excellent overall yield from commercially available *cis*-2-butene-1,4-diol, was first treated with sodium phenylthiolate, generated in situ from thiophenol and sodium hydride, to give the racemic *trans*-alcohol (±)-**2**, which gave the racemic acetate (±)-**3** in nearly quantitative yield on acetylation (Scheme 1). On treatment with two equivalents of vinyl acetate in diisopropyl ether in the presence of lipase[4] PS (*Pseudomonas* sp., Amano)-on-Celite [10 mg/mmol of (±)-**2**], the racemic alcohol (±)-**2** afforded the (+)-acetate (*R,R*)-**3** in 49.1% yield, leaving the unchanged (−)-alcohol (*S,S*)-**2** in 48.9% recovery, after stirring for 12 d at 30 °C (Scheme 2). The former product gave the (+)-alcohol (*R,R*)-**2** in 96.6% yield on methanolysis in the presence of potassium carbonate. At this point the absolute configuration of the products could not be determined. However, their optical purities were determined by HPLC analysis of both enantiomers of the alcohol **2** using a chiral column (CHIRALCEL OD) to be more than 99% ee.



Scheme 1

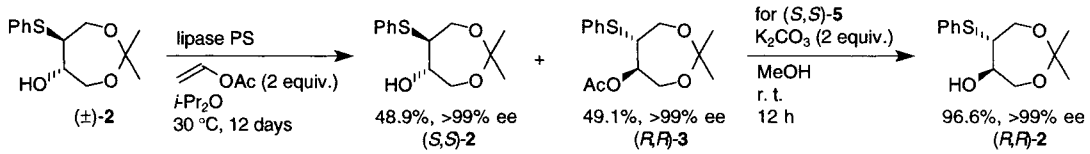
On the other hand, the kinetic resolution of the racemic acetate (±)-**3** in a phosphate buffer medium in the presence of the same lipase[4] failed to give the optically active products in a practical level of optical purity owing to the uncontrollable reaction rate.

To determine the absolute configuration, the (−)-alcohol (*S,S*)-**2** was stirred with an ion-exchange resin (acid form) in methanol to give the sulfide triol (*S,S*)-**4** in 78.3% yield after recrystallization. This compound was then refluxed with Raney nickel (W-2) to give the triol (*R*)-**5** which was found to be enantiomeric with the (*S*)-triol (*S*)-**5** obtained from (*S*)-malic acid.[1,5] Thus, the absolute structures of the optically active products obtained above were determined as shown.

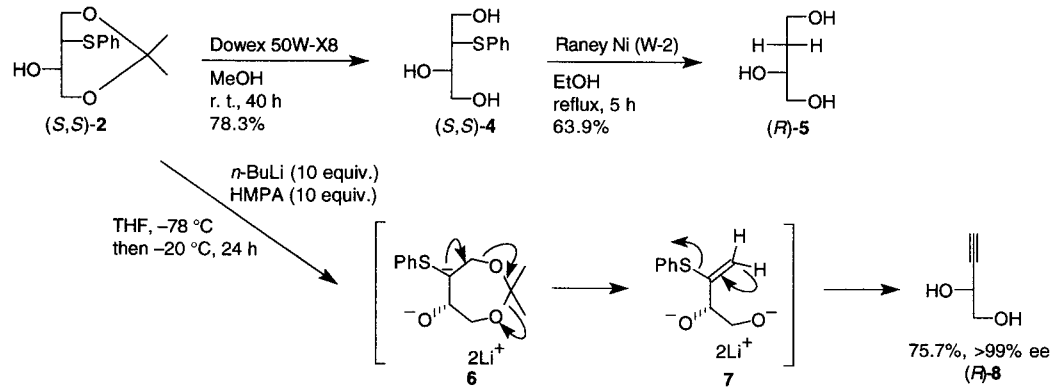
Having established the stereochemistry, the (−)-alcohol (*S,S*)-**2** was exposed to 10 equiv of butyllithum[6] in the presence of 10 equiv of hexamethylphosphoric triamide (HMPA) in THF[7] to afford the acetylenic four-carbon diol[7,8] (*R*)-**8** in 75.7% yield whose optical purity was determined to be more than 99% ee by HPLC analysis using a chiral column (CHIRALCEL OD) after transformation into the dibenzyl ether. Thus, the original optical integrity of the starting material (*S,S*)-**2** was preserved under these strong basic conditions[9] owing to the presence of the secondary hydroxy group which directs the regioselective elimination and prevents the racemization via sequential generation of dianion intermediates **6** and **7** (Scheme 3).

To demonstrate its utility, the acetylenediol (*R*)-**8** was transformed into the butenolide[10] (*R*)-**13** which has proved to be a versatile chiral building block.[11] Thus, (*R*)-**8** was first transformed into the acetonide **9** which was sequentially treated with butyllithium and methyl chloroformate to give the ester[12] **10** in a satisfactory yield. After removal of the acetonide group, the resulting acetylenediol **11** was hydrogenated to give the *Z*-olefin diol **12** which on acid treatment afforded (*R*)-4-hydroxymethyl-2-butenolide [(*R*)-**13**] in 57% overall yield from (*R*)-**8** (Scheme 4).

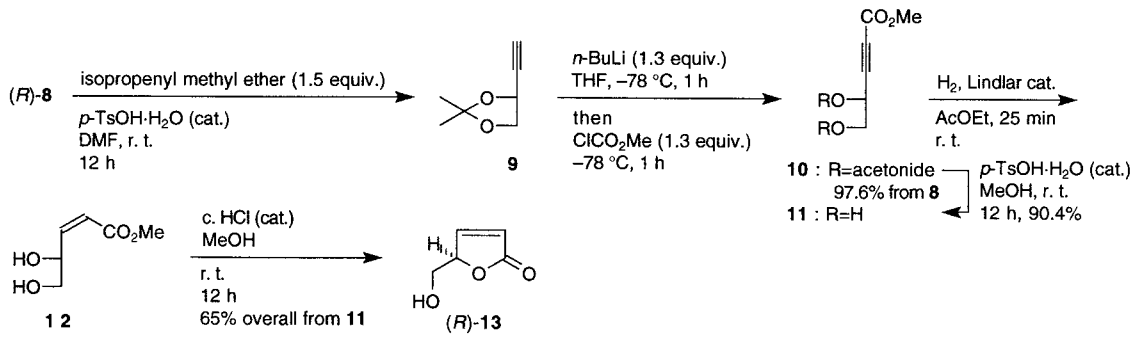
In conclusion, we have established an efficient lipase-mediated procedure for the conversion of a readily accessible *meso*-symmetric epoxide into three optically pure four-carbon di- and triol molecules in both enantiomeric forms. The present procedure, as well as the optically pure products thus obtained, may be useful for the construction of a wide variety of optically active materials.



Scheme 2



Scheme 3



Scheme 4

IR spectra were recorded on a JASCO-IR-700 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-3000 (300 MHz) spectrometer. Optical rotations were measured with a JASCO-DIP-370 digital polarimeter. Optical purities were determined on a Gilson Model-307 instrument equipped with a chiral column. Compounds (±)-**2**, (±)-**3**, (2*S*,3*S*)-**4**, **8**-di(benzyl ether) and **11** gave C, H (S where appropriate) analysis ±0.18%.

Racemic (2*R,3*R**)-1,4-Di-*O*-isopropylidene-3-phenylthio-1,2,4-butanetriol [(±)-2]:**

To a stirred suspension of sodium hydride (2.14 g, 89.1 mmol) in THF (300 mL) was added dropwise thiophenol (2.14 g, 89.1 mmol) at 0 °C. After 30 min, the epoxide[3] **1** (9.79 g, 74.1 mmol) in THF (100 mL) at 0 °C was added dropwise and the mixture was stirred at the same temperature for 30 min, then refluxed for 1 h. After cooling, water (100 mL) was added and the mixture was extracted with Et_2O (2 × 300 mL). The combined extract was washed with brine (100 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (silica gel, 300 g; EtOAc/hexane, 1:4) to give (±)-**2** as a colorless oil; yield: 17.4 g (96.9%).

IR (neat): ν = 3700–3100 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.39–7.47 (m, 2H), 7.20–7.34 (m, 3H), 4.00–4.10 (m, 1H), 3.98 (dd, 1H, J = 12.8, 2.5 Hz), 3.75 (dd, 1H, J = 12.8, 6.2 Hz), 3.56–3.68 (m, 2H), 3.08–3.20 (m, 1H), 2.82 (d, 1H, J = 5.8 Hz, exch. with D_2O), 1.35 (s, 6H).

MS: m/z = 254 (M^+), 110 (100%).

HRMS: m/z calc. for $C_{13}H_{18}O_3S$, 254.0977; found, 254.0970.

Racemic (2*R,3*R**)-2-Acetoxy-1,4-di-*O*-isopropylidene-3-phenylthio-1,4-butanediol [(±)-3]:**

To a stirred solution of (±)-**2** (1.91 g, 7.51 mmol) in CH_2Cl_2 (40 mL), Ac_2O (1.06 mL, 11.2 mmol), Et_3N (1.57 mL, 11.2 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) were added sequentially at 0 °C and the mixture was stirred at r.t. for 5 h. The mixture was treated with sat. aq $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (100 mL × 2). The extract was washed with brine (50 mL × 2), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (silica gel, 70 g; EtOAc/hexane, 1:9) to give (±)-**3** as a colorless oil; yield: 2.20 g (98.8%).

IR (neat): ν = 1740 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.40–7.50 (m, 2H), 7.19–7.34 (m, 3H), 4.85 (td, 1H, J = 5.8, 1.8 Hz), 3.96–4.10 (m, 2H), 3.66–3.80 (m, 2H), 3.27 (td, 1H, J = 5.4, 1.5 Hz), 2.07 (s, 3H), 1.35 (s, 6H).

MS: m/z = 296 (M^+), 110 (100%).

HRMS: m/z calc. for $C_{15}H_{20}O_4S$, 296.1082; found, 296.1082.

Lipase-Mediated Kinetic Acylation; (2*R*,3*R*)-(+)-2-Acetoxy-1,4-di-*O*-isopropylidene-3-phenylthio-1,4-butanediol [(2*R*,3*R*)-3] and (2*S*,3*S*)-(−)-2-Hydroxy-1,4-di-*O*-isopropylidene-3-phenylthio-1,4-butanediol [(2*S*,3*S*)-2]:

A suspension of (±)-**2** (5.38 g, 21.1 mmol), vinyl acetate (3.89 mL, 42.2 mmol), and lipase PS-on-Celite (*Pseudomonas* sp., Amano, 2.11 g) in *i*-Pr_2O (50 mL) was stirred at 30 °C for 12 d. After filtration through a Celite pad, the filtrate was evaporated under reduced pressure and chromatographed (silica gel, 200 g) to give the acetate (2*R*,3*R*)-**3** from the less polar eluent (EtOAC/hexane, 1:9) and the alcohol (2*S*,3*S*)-**2** from the more polar eluent (EtOAc/hexane, 1:4).

(2*R*,3*R*)-**3**: colorless oil, yield: 3.08 g (49.1%), $[\alpha]_D^{28}$ + 35.5° (c = 1.0, $CHCl_3$). Spectral data and chromatographic behavior were identical with those of (±)-**3**.

(2*S*,3*S*)-**2**: colorless oil, yield: 2.63 g (48.9%), $[\alpha]_D^{31}$ − 20.4° (c = 1.6, $CHCl_3$) (> 99% ee by HPLC using CHIRALCEL OD; *i*-PrOH/hexane, 5:95). Spectral data and chromatographic behavior were identical with those of (±)-**2**.

Deacylation of the Acetate (2*R*,3*R*)-3 to the Alcohol (2*R*,3*R*)-2:

A suspension of (2*R*,3*R*)-**3** (1.35 g, 4.56 mmol) and K_2CO_3 (1.26 g, 9.12 mmol) in MeOH (23 mL) was stirred at r.t. for 12 h. After filtration through a Celite pad, the mixture was evaporated under reduced pressure and chromatographed (silica gel, 50 g; EtOAc/hexane, 1:4) to give (2*R*,3*R*)-**2** as a colorless oil; yield: 1.12 g (96.6%), $[\alpha]_D^{34}$ − 34.1° (c = 1.1, $CHCl_3$) (> 99% ee by HPLC using CHIRALCEL OD; *i*-PrOH/hexane, 5:95). Spectral data and chromatographic behavior were identical with those of (±)-**2**.

(2*S*,3*S*)-3-Phenylthio-1,2,4-butanetriol [(2*S*,3*S*)-4]:
A suspension of (2*S*,3*S*)-**2** (262 mg, 1.03 mmol) and Dowex 50W-X8 (26 mg) in MeOH (5 mL) was stirred at r.t. for 40 h. After filtration through a Celite pad, the mixture was evaporated under reduced pressure to leave a crystalline solid which was recrystallized from CH_2Cl_2 to give pure (2*S*,3*S*)-**4** as colorless needles, yield: 173 mg (78.3%), mp 92–93°C; $[\alpha]_D^{27}$ + 16.4° (*c* = 1.0, MeOH).

IR (Nujol): $\nu = 3500-3100\ cm^{-1}$.

^1H NMR (acetone-d_6): δ = 7.40–7.49 (m, 2H), 7.24–2.32 (m, 2H), 7.15–7.23 (m, 1H), 4.06–4.18 (m, 2H), 1H exch. with D_2O), 3.98–4.05 (m, 1H, exch. with D_2O), 3.72–3.90 (m, 5H, 1H exch. with D_2O), 3.39–3.47 (m, 1H).

MS: *m*/*z* = 214 (M^+), 136 (100%).

HRMS: *m*/*z* calc. for $C_{10}H_{14}O_3S$, 214.0664; found 214.0624.

(2*R*)-1,2,4-Butanetriol [(*R*)-5]:
A suspension of (2*S*,3*S*)-**4** (304 mg, 1.42 mmol) and Raney Ni (W-2, ca. 1.2 g) in EtOH (5 mL) was refluxed for 5 h. After cooling, the mixture was filtered through a Celite pad and the filtrate was evaporated under reduced pressure. The residue was chromatographed (silica gel, 15 g; MeOH/CH_2Cl_2, 1:9) to give (*R*)-**5** as a colorless oil, yield: 96.3 mg (63.9 g), $[\alpha]_D^{27}$ + 27.9° (*c* = 0.77, MeOH) {Lit.[5b] $[\alpha]_D$ − 29° (*c* = 1.03, MeOH) for (*S*)-**5**}. Spectral data were identical with those reported.[5c]

(*R*)-1-Butyne-3,4-diol [(*R*)-8] from (2*S*,3*S*)-2:
To a stirred solution of (2*S*,3*S*)-**2** (507 mg, 1.99 mmol) and HMPA (3.46 mL, 19.9 mmol) in THF (19.9 mL) was added BuLi (1.56 M in hexane, 12.8 mL, 19.9 mmol) at − 78°C, the temperature was raised to − 20°C and the mixture was stirred at the same temperature for 24 h. After having quenched the reaction by addition of sat. aq NH_4Cl (50 mL), the mixture was extracted with EtOAc (200 mL × 8), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (silica gel, 30 g; EtOAc/hexane, 2:3) to give (*R*)-**8** as colorless needles, yield: 130 mg (75.5%), mp 36–38°C; $[\alpha]_D^{27}$ − 37.4° (*c* = 1.1, $CHCl_3$) {Lit. $[\alpha]_D^{24}$ − 37.8° (*c* = 1.0, $CHCl_3$) for (*R*)-**8**,[7] mp 34–35°C. $[\alpha]_D^{25}$ + 35.5° (*c* = 1.07, $CHCl_3$) for (*S*)-**8**,[8] mp 36–38°C. $[\alpha]_D^{24}$ − 37.8° (*c* = 1.0, $CHCl_3$) for (*R*)-**8**[9]}. Spectral data were identical with those reported.[8]

Determination of the Optical Purity of (*R*)-8 by Transformation into the Dibenzyl Ether:
To a stirred suspension of NaH (42.6 mg, 1.77 mmol) in DMF (3 mL) was added dropwise (*R*)-**8** (61.2 mg, 0.71 mmol) in THF (3 mL) at 0°C. After stirring at r.t. for 1 h, the mixture was cooled to − 30°C and benzyl bromide (0.21 mL, 1.77 mmol) was added dropwise. After stirring at r.t. for 1 h, the reaction was quenched by addition of water (0.5 mL) and the mixture was diluted with Et_2O (100 mL). The organic layer was washed with brine (2 × 20 mL), dried ($MgSO_4$), evaporated under reduced pressure, and chromatographed (silica gel, 20 g; Et_2O/hexane, 1:19) to give (*R*)-3,4-di-*O*-benzyl-1-butyne-3,4-diol as a colorless oil; yield: 180 mg (95.1%), $[\alpha]_D^{30}$ − 84.0° (*c* = 1.20, $CHCl_3$) (> 99% ee by HPLC using CHIRALCEL OD; *i*-PrOH/hexane, 1:99).

IR (film): $\nu = 3288, 2112\ cm^{-1}$.

^1H NMR ($CDCl_3$): δ = 7.26–7.41 (m, 10H), 4.84 (d, 1H, *J* = 11.7 Hz), 4.64 (d, 1H, *J* = 12.0 Hz), 4.59 (d, 1H, *J* = 13.5 Hz), 4.58 (d, 1H, *J* = 12.0 Hz), 4.33 (ddd, 1H, *J* = 6.6, 4.6, 2.2 Hz), 3.72 (dd, 1H, *J* = 10.4, 6.2 Hz), 3.67 (dd, 1H, *J* = 10.6, 4.7 Hz), 2.49 (d, 1H, *J* = 2.2 Hz).

MS: *m*/*z* = 226 (M^+), 91 (100%).

HRMS: *m*/*z* calc. for $C_{18}H_{18}O_2$, 266.1307; found, 266.1339.

Methyl (*R*)-4,5-Di-*O*-isopropylidene-4,5-dihydroxy-2-butynoate [(*R*)-10]:
A solution of (*R*)-**8** (522 mg, 6.07 mmol) and 2-methoxypropene (0.76 mL, 7.89 mmol) in DMF (15 mL) containing *p*-TsOH · H_2O (57.7 mg, 0.303 mmol) was stirred at r.t. for 12 h. After dilution with Et_2O (200 mL), the mixture was washed with sat. aq $NaHCO_3$ (50 mL) and brine (30 mL × 2), dried ($MgSO_4$) and evaporated under atmospheric pressure to leave the acetonide **9** as a volatile oil which was immediately used for the next reaction.

Compound **9** was dissolved in THF (30 mL) and cooled to − 78°C with stirring. To this stirred mixture was added dropwise BuLi (1.56 M in hexane: 5.06 mL, 7.89 mmol) at the same temperature, then, after stirring at the same temperature for 1 h, methyl chloroformate (0.609 mL, 7.89 mmol) was added dropwise. After stirring for further 1 h at the same temperature, the reaction was quenched by addition of sat. aq $NaHCO_3$ (20 mL) and extracted with Et_2O (2 × 100 mL). The extract was washed with brine (40 mL), dried ($MgSO_4$), evaporated under reduced pressure, and chromatographed (silica gel, 50 g; EtOAc/1:19) to give (*R*)-**10** as a colorless oil, yield: 1.09 g (97.6%), $[\alpha]_D^{25}$ − 83.8° (*c* = 1.1, benzene) {Lit.[12] $[\alpha]_D$ + 56.4° (*c* = 19.5, benzene) for *S*-enantiomer}. Spectral data were identical with those reported for the *S*-enantiomer.[12]

Methyl (*R*)-4,5-Dihydroxy-2-butynoate [(*R*)-11]:
A solution of (*R*)-**10** (154 mg, 0.837 mmol) in MeOH (4 mL) containing *p*-TsOH · H_2O (7.9 mg, 41.5 μmol) was stirred at r.t. for 12 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (50 mL), washed with sat. aq $NaHCO_3$ (20 mL × 2) and dried ($MgSO_4$). After evaporation of the solvent, the residue was chromatographed (silica gel, 15 g; EtOAc/hexane, 3:2) to give (*R*)-**11** as colorless needles, yield: 109 mg (90.4%), mp 47–49°C; $[\alpha]_D^{29}$ − 34.5° (*c* = 1.0, $CHCl_3$).

IR (film): $\nu = 3600-3100, 2240, 1712\ cm^{-1}$.

^1H NMR ($CDCl_3$): δ = 4.58 (td, 1H, *J* = 6.0, 4.0 Hz), 3.75–3.85 (m, 2H), 3.79 (s, 3H), 2.74–2.84 (m, 1H, exch. with D_2O), 2.28–2.38 (m, 1H, exch. with D_2O).

MS: *m*/*z* = 145 ($M^+ + 1$), 114 (100%).

HRMS: *m*/*z* calc. for $C_6H_9O_4$, 145.0501; found, 145.0496.

(*R*)-4-Hydroxymethylbut-2-en-4-olide [(*R*)-13]:
A solution of (*R*)-**11** (340 mg, 2.36 mmol) in EtOAc (10 mL) was hydrogenated under atmospheric pressure in the presence of Lindlar catalyst (34 mg) at r.t. After 25 min, the suspension was filtered through a Celite pad and the filtrate was evaporated under reduced pressure to leave crude *Z*-ester **12**. The residue was dissolved in MeOH (14 mL) containing conc. aq HCl (4.5 mL) and the solution was stirred at r.t. for 12 h. After evaporation of the solvent under reduced pressure, the residue was dissolved in EtOAc (200 mL) and the solution was washed with sat. aq $NaHCO_3$ (40 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (silica gel, 20 g; EtOAc/hexane, 3:2) to give (*R*)-**13** as a colorless oil, yield: 175 mg (65%), $[\alpha]_D$ − 143.2° (*c* = 1.6, H_2O) {Lit. $[\alpha]_D^{20}$ − 145° (*c* = 0.13, H_2O);[10a] $[\alpha]_D^{24}$ − 136.3° (*c* = 0.25, H_2O)[10b]}. Spectral data were identical with those reported.[10b]

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