w, 2995 m, 2948 m, 2880 m, 1722 w, 1629 s, 1589 m, 1480 m, 1449 s, 1429 m, 1415 m, 1387 m, 1306 s, 1240 s, 1209 s, 1148 s, 1073 s, 1027 s, 1000 s, 937 s, 828 s. ^{1}H NMR (200 MHz): 7.88–7.83 (m, 2 H, Ar H ortho to SO_2), 7.66–7.46 (m, 3 H, Ar H), 5.71–5.52 (m, 1 H, C*H*=CH_2), 5.14–5.04 (m, 2 H, CH=CH_2), 4.24 (d, J = 3.0, 1 H, C=C*H*H), 4.13 (d, J = 3.0, 1 H, C=CH*H*), 4.02 (dxd, J = 12.6, 5.4, 1 H, OCH_aH_b), 3.91 (dxd, J = 12.6, 5.4, 1 H, OCH_aH_b), 3.79 (q, J = 7.2, 1 H, SO_2CHCH_3), 1.57 (d, J = 7.2, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 252 (M^+, 0.49), 111 (12), 110 (33), 91 (11), 83 (12), 81 (10), 78 (11), 77 (54), 69 (12), 55 (56), 53 (18), 51 (32), 43 (52), 41 (100). Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.90; H, 6.35; S, 12.70. Found: C, 61.79; H, 6.60, S, 12.76.

1-[[1-Methyl-2-[(1-methyl-2-propenyl)oxy]-2-propenyl]-sulfonyl]benzene (1ie). Method B. Chromatography solvent, hexane/EtOAc, 4/1. Yield, 88%. Though chromatographically homogeneous, the compound consisted of a mixture of two β,γ-unsaturated isomers and one α,β-unsaturated isomer in a ratio of 40:40:20. IR (neat): 3071 w, 2990 w, 2940 w, 1712 w, 1622 w, 1588 w, 1479 w, 1448 m, 1420 w, 1372 w, 1305 s, 1290 s, 1248 m, 1207 w, 1148 s, 1072 m, 1071 w, 998 m, 989 m, 930 w, 895 w, 817 m. ^{1}H NMR (200 MHz): 7.89–7.46 (m, 5 H, Ar H, all isomers), 5.89–5.39 (m, 1 H, C*H*=CH_2, all isomers), 5.20–4.97 (m, 2 H, CH=CH_2, all isomers), 4.75 (quintet, J = 6.7, 1 H, $OCHCH_3$, α,β isomer), 4.34–4.17 (m, 1 H, $OCHCH_3$, 1st β,γ isomer), 4.20 (d, J = 3.0, 1 H, C=C*H*H, β,γ isomers), 4.18 (d, J = 3.0, 1 H, C=CH*H*, 1st β,γ isomer), 4.12 (d, J = 3.0, 1 H, C=C*H*H, 2nd β,γ isomer), 4.09 (d, J = 3.0, 1 H, C=CH*H*, 2nd β,γ isomer), 3.82–3.67 (m, 1 H, $PhSO_2CHCH_3$, β,γ isomers), 2.42 (q, J = 1.4, 3 H, =C(CH_3), α,β isomer), 1.92 (q, J = 1.4, 3 H, $O(CH_3)C$=C, α,β isomer), 1.56 (d, J = 7.2, 3 H, SO_2CHCH_3, β,γ isomer), 1.54 (d, J = 7.1, 2 H, $PhSO_2CHCH_3$, β,γ isomer), 1.33 (d, J = 6.3, 3 H, $OCHCH_3$, α,β isomer), 1.13 (d, J = 6.4, 3 H, $OCHCH_3$, β,γ isomer), 0.97 (d, J = 6.4, 3 H, $OCHCH_3$, β,γ isomer). MS (10 eV): m/e (relative intensity) 266 (M^+, 1.3), 212 (21), 145 (14), 143 (22), 126 (27), 125 (51), 124 (57), 109 (20), 105 (12), 81 (12), 78 (16), 77 (10), 71 (88), 69 (13), 57 (18), 55 (97), 53 (21), 43 (100). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.16; H, 6.77; S, 12.03. Found: C, 63.13; H, 6.83; S, 11.93.

(*E*)-3,3-Dimethyl-1-[(4-methylphenyl)sulfonyl]-5-hepten-2-one (8ce). Method B. This compound was formed during workup. Chromatography solvent, hexane/EtOAc, 4/1. Yield, 87%. IR ($CHCl_3$): 3029 s, 3019 m, 2971 m, 2938 w, 2920 w, 2880 w, 1717 s, 1648 w, 1492 w, 1468 m, 1450 w, 1439 w, 1401 w, 1389 w, 1380 w, 1368 w, 1326 s, 1306 m, 1292 m, 1230 m, 1226 m, 1211 s, 1208 m, 1187 w, 1152 s, 1119 w, 1087 m, 1070 w, 1037 m, 1018 m, 1004 m, 970 m, 955 w, 927 w, 875 w, 812 m. ^{1}H NMR (200 MHz): 7.83 (d, J = 8, 2 H, Ar H ortho to SO_2), 7.36 (d, J = 8, 2 H, Ar H), 5.46–5.36 (m, 1 H, C*H*=CH), 5.22–5.12 (m, 1 H, CH=C*H*), 4.27 (s, 2 H, p-$TolSO_2CH_2$), 2.45 (s, 3 H, $C_6H_4CH_3$), 2.12 (d, J = 7, 2 H, CH_2), 1.60 (d, J = 7, 3 H, =$CHCH_3$), 1.11 (s, 6 H, 2 × CH_3). MS (70 eV): m/e (relative intensity) 294 (M^+, 3), 240 (50), 222 (20), 155 (13), 139 (20), 138 (16), 121 (27), 97 (41), 95 (19), 92 (13), 91 (51), 85 (26), 81 (15), 69 (51), 67 (22), 65 (24), 57 (11), 55 (100), 53 (10), 44 (41), 43 (47), 39 (22). Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.31; H, 7.48; S, 10.80. Found: C, 65.40; H, 7.91; S, 11.02.

1-[[3-Methyl-1-[2-methyl-1-[[(4-methylphenyl)sulfonyl]-methyl]-1-propenyl]-1,2-propadienyl]sulfonyl]-4-methyl-benzene (9). Method B. Chromatography solvent, hexane/EtOAc, 3/1. Yield, 76%; mp 142–144 °C. IR ($CHCl_3$): 2995 w, 2970 w, 2900 w, 2840 w, 1950 w, 1905 w, 1648 w, 1599 m, 1490 w, 1385 w, 1357 m, 1310 s, 1298 s, 1282 s, 1260 w, 1235 w, 1180 w, 1145 s, 1119 w, 1085 s, 1070 w, 1040 w, 1020 w, 950 w, 899 w, 815 w. ^{1}H NMR (220 MHz): 7.72 (d, J = 8.4, 2 H, Ar H ortho to SO_2), 7.71 (d, J = 8, 2 H, Ar H ortho to SO_2), 7.32 (d, J = 8, 2 H, Ar H), 7.30 (d, J = 8.2, 2 H, Ar H), 4.23 (s, 2 H, p-$TolSO_2CH_2$), 2.44 (s, 6 H, 2 × $C_6H_4CH_3$), 1.75 (s, 6 H, =CCH_3), 1.54 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3). MS (70 eV): m/e (relative intensity) 289 (M^+ – 189, 25), 225 (11), 157 (21), 149 (13), 139 (28), 133 (100), 132 (42), 117 (31), 115 (16), 105 (49), 93 (14), 92 (20), 91 (81), 79 (21), 77 (34), 65 (31), 55 (12), 51 (12), 44 (44), 43 (13). Anal. Calcd for $C_{24}H_{28}O_4S_2$: C, 64.86; H, 6.31; S, 14.41. Found: C, 64.54; H, 6.41; S, 14.43.

Acknowledgment. We gratefully acknowledge the financial support for this project by grants from the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. M.A.H. thanks the University of Illinois and the Eastman Kodak Company for financial support in the form of graduate fellowships. This work was supported in part by the University of Illinois Mass Spectrometry Laboratory (PHS HHS GM-27029). Dr. Nancy L. Sear is thanked for the modified preparation of **1ag** and **2ag**.

A Combined Microbial/Chemical Synthesis of (+)-(*R*)-Methyloxirane Having High Enantiomeric Excess[1]

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Received April 8, 1987

Clostridium thermosaccharolyticum (ATCC 31960) converts glucose to (–)-(*R*)-propylene glycol; standard procedures transform this substance to (+)-(*R*)-methyloxirane ((+)-(*R*)-propylene oxide) with enantiomeric excess >99%. This procedure is capable of generating this useful chiral synthon on a large scale.

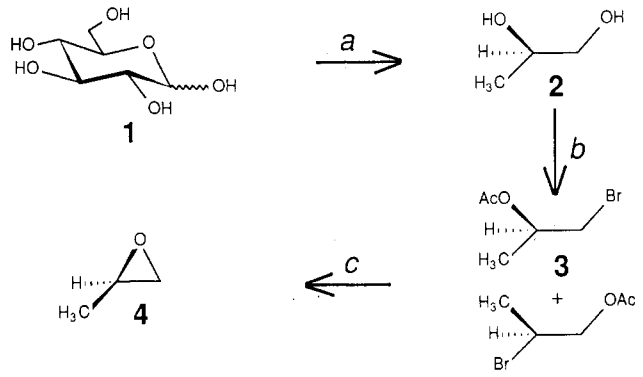
Enantiomerically pure (+)-(*R*)-methyloxirane (**4**) is a valuable chiral synthon.[2-4] This paper details a new method for the production of multigram quantities of optically pure (>99% ee) **4** from glucose (**1**) (Scheme I). Previous syntheses of this substance have started with ethyl (+)-(*S*)-lactate,[5,6] alanine,[7,8] propene,[9] and acetol.[10] Methods developed for butene oxide could also be applied to **4**.[11]

[†] 1986–1987 Du Pont Fellow.

(1) This research was supported by grants from the National Institutes of Health (GM 30367, to G.M.W.) and from the Solar Energy Research Institute (DOE Contract DE-AC02-83CH10093, Subcontract XX-3-03058-01, to C.L.C.). The 300-MHz NMR instrument was supported in part by the National Science Foundation, BRS Shared Instrumentation Grant Program (1 S10 RR01748-01A1).

0022-3263/87/1952-4042$01.50/0

Scheme I. Preparation of Enantiomerically Pure (+)-(R)-Methyloxirane[a]



[a] Key: (a) *C. thermosaccharolyticum*, 60 °C, 37 h (7.9 g/L); (b) HBr/AcOH, room temperature (82%); (c) $C_5H_{11}OK$, $C_5H_{11}OH$, room temperature (88%).

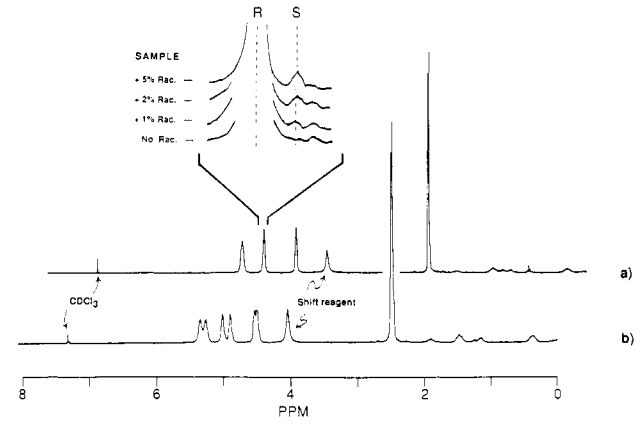


Figure 1. ^1H NMR spectra of **4** (a) and of racemic methyloxirane (b) in the presence of Eu(tfc). Addition of racemic methyloxirane to **4** (expansion) allowed the quantitative determination of percent ee.

Fermentation of glucose in a glass carboy by the bacterium *Clostridium thermosaccharolyticum* (ATCC 31960)[12] yielded an aqueous broth containing 7.9 g/L of (−)-(*R*)-1,2-propanediol (**2**). Concentration and filtration of the broth, continuous extraction into ether, and distillation yielded **2** with an enantiomeric excess of >99%, as measured by ^1H NMR in the presence of Eu(tfc).[13]

Reaction of **2** with hydrobromic acid in acetic acid afforded a mixture of acetoxybromopropanes, of which the major compound was **3**. Treatment of this mixture with potassium pentanolate[14] in pentan-1-ol generated the epoxide **4**. The enantiomeric excess of **4**, measured by ^1H NMR spectroscopy in the presence of Eu(hfc), was >99% (Figure 1). The shift reagent studies were calibrated by the sequential addition of precisely determined amounts of either the opposite enantiomer or the racemic material to a known amount of the sample.

This procedure has several advantages over existing methods. The starting material, glucose, is readily available; other sugars such as xylose and mannose may also be used.[12] The enantiomeric excess of the product is high. The procedure can be used to produce **4** on a large scale.

Experimental Section

Materials and Methods. Infrared spectra were recorded as neat films on NaCl plates. Optical rotations were measured in a 1-dm cell with a Perkin-Elmer 241 polarimeter. The lanthanide shift studies were carried out with a Bruker AM 300 instrument. Concentrations of glucose, 1,2-propanediol, acetate, lactate, and ethanol in aqueous solution were measured by HPLC (column, AMINEX HPX87H, Bio-Rad Laboratories; solvent, 0.005 M H_2SO_4; flow rate, 0.5 mL/min; column temperature, 45 °C; refractive index detection).

C. thermosaccharolyticum (ATCC 31960) is available from the American Type Culture Collection. This microorganism is nonpathogenic. Yeast extract was obtained from DIFCO. Deuteriated acetonitrile (1% Me_4Si) was purchased from ICN Biomedical, Inc. Eu(tfc) was dried in vacuo in a drying pistol at 50 °C and manipulated under a nitrogen atmosphere. All other chemicals and biochemicals were reagent grade and were used without further purification.

Analysis of Optical Purity. The splitting of enantiotopic protons of **2** in the presence of Eu(tfc) was monitored by ^1H NMR spectroscopy, with CD_3CN as a solvent.[15] Calibration of the shift study was as follows. Separate standard solutions of the sample and of the *S* enantiomer were made in volumetric flasks. A precise amount of the standard solution containing the sample was added via syringe into a dry NMR tube, followed by addition of the shift reagent. Precisely determined amounts of the standard solution containing the *S* enantiomer were then added by syringe; continued addition of the solution increased the intensity of the signals corresponding to the *S* enantiomer, which were resolved at the base line from those corresponding to the *R* enantiomer. Signals corresponding to the *S* enantiomer were not observed with the standard solution containing the sample but were observed when the ratio of the sample standard solution to the *S* enantiomer standard solution was 99.5:0.5. Drying the commercially obtained shift reagent enhanced resolution. For compound **4**, Eu(hfc) in $CDCl_3$ was used as the lanthanide shift reagent. Stepwise addition, as above, of precise amounts of racemic material calibrated the study.

Fermentation of Glucose.[16] Solutions containing the following compounds were prepared in distilled water and were autoclaved at 121 °C for 30 min: (1) 7.0 g of NaCl, 10.4 g of $MgCl_2 \cdot 6H_2O$, 0.9 g of $CaCl_2 \cdot H_2O$, and 14 mg of sodium resazurin (a redox indicator) in a total volume of 0.7 L; (2) 35.0 g of yeast extract, 20.3 g of K_2HPO_4, 10.5 g of KH_2PO_4, 9.1 g of $(NH_4)_2SO_4$, 35 mg of $FeSO_4 \cdot 7H_2O$ in a total volume of 0.7 L; (3) 315 g of D-glucose in a total volume of 0.7 L; (4) 119 g of $NaHCO_3$ and 3.5 g of L-cysteine hydrochloride in a total volume of 4.2 L. Solution 4 was prepared in a 5-gal Pyrex carboy sealed with a three-holed rubber stopper containing three stainless steel tubes; one tube served as an entrance port for CO_2, one was attached to a paraffin oil bubbler to allow the escape of H_2 and CO_2 during the fermentation, and one was a sampling port. The solutions were cooled to below 45 °C, and then the first three solutions were added aseptically to the carboy. The carboy was sparged with CO_2 for 20 min or until the disappearance of the red color, due to the oxidized form of resazurin, indicated that the medium was free of oxygen. The carboy was then heated to 60 °C in an incubator and inoculated with 0.7 L of a vigorous culture of *C. thermosaccharolyticum* grown in an anaerobic flask[17] containing

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the above medium. The fermentation was stopped after 37 h at which time analysis by HPLC indicated 7.9 g/L of **2**; acetate, lactate, and ethanol were also produced.[18]

In practical use, the addition of resazurin and the analysis by HPLC are not necessary. To accommodate foaming, a 5-gal carboy should contain no more than 15 L of medium. The periodic addition of antifoam (FG-10, Dow-Corning, concentration ≤0.5 g/L) can control foaming.

Purification of (−)-(*R*)-1,2-Propanediol (2). Centrifugation (4000*g*, 25 min) of the cell suspension resulting from a 5-L fermentation separated the cell mass from the broth. The broth was concentrated to 880 mL by rotary evaporation at 0.1 Torr after the addition of 0.1 mL/L of silicon antifoam (FG-10, Dow-Corning). Overnight storage of the concentrate at 4 °C precipitated salts and protein that were removed by centrifugation. Buchner filtration of the concentrate and passage through a 0.45-μm filter prevented the formation of an emulsion during the subsequent continuous extraction into ether. After 120 h of continuous extraction (water:ether ≃ 1:1.4, v:v), concentration of the ethereal phase yielded 31 g of crude **2**, which was distilled at reduced pressure to yield 23 g (0.3 mol) of a clear, viscous liquid: ee >99%; $[\alpha]^{23}_D$ −22.0° (*c* 7.5, H_2O) [lit.[19] $[\alpha]^{20}_D$ −22.2° (*c* 7.5, H_2O)]; ^1H NMR spectrum agreed with that of the *S* enantiomer.[13] Further continuous extraction yielded an additional 12 g of crude **2** after nine more days.

(+)-(*R*)-Methyloxirane (4). Conversion of the diol to the epoxide proceeded via the acetoxybromopropanes according to published procedures.[13] Thus, from 25.0 g (330 mmol) of **2** was obtained 48.7 g (270 mmol, 82%) of a clear, colorless liquid whose ^1H NMR spectrum[13] identified it as mainly **3**; ^1H NMR spectroscopy indicated the presence of approximately 6% of 1-acetoxy-2-bromopropane. Conversion of the mixture (25.0 g, 138 mmol) to **4** by treatment with potassium pentanolate in pentan-1-ol followed the literature[13] to yield 6.8 g (121 mmol, 88%) of **4** as a clear, colorless liquid: bp 38–39 °C (lit.[13] bp 34–35 °C); ee >99%; $[\alpha]^{22}_D$ +18.0° (*c* 5.73, CCl_4) [(lit.[13] $[\alpha]^{18}_D$ +19.13° (*c* 5.66, CCl_4)]; ^1H NMR spectral data were in agreement with those in the literature.[13]

Registry No. **1**, 50-99-7; **2**, 4254-14-2; **3**, 99457-42-8; **4**, 15448-47-2; (*S*)-$H_3CCHBrCH_2OAc$, 109243-62-1.

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Synthesis of Functionalized Bicyclic Dioxopiperazines via Intramolecular Epoxide Opening

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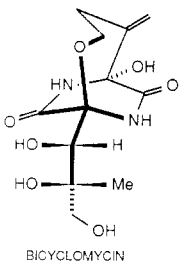
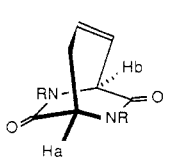
Received March 3, 1987

d,l-Homoserine was condensed with *N*-*p*-methoxybenzylglycine ethyl ester and alkylated to furnish (2-hydroxyethyl)piperazinedione **8**. Oxidation to the corresponding aldehyde and condensation with dimethylsulfoxonium methylide provided the epoxide **10**. Enolate formation resulted in an intramolecular epoxide opening reaction providing the bicyclo[2.2.2] (**11**) and bicyclo[3.2.2] (**12**) dioxopiperazines in a 3:1 ratio. Dehydration of **11** and **12** provided 6,8-bis(*p*-methoxybenzyl)-2-methylene-6,8-diazabicyclo[2.2.2]octane-5,7-dione (**2**) and 7,9-bis(*p*-methoxybenzyl)-7,9-diazabicyclo[3.2.2]non-2-ene-6,8-dione (**1**), respectively.

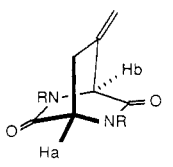
As part of a program directed at synthesizing and studying unnatural analogues of the natural antibiotic bicyclomycin,[1] the carbocyclic bicyclo[3.2.2] and bicyclo[2.2.2] olefins **1** and **2** were chosen as potentially interesting targets. It was reasoned that omission of the bridging ether oxygen in the more highly strained bicyclo[3.2.2] and -[2.2.2] ring systems would impart both increased chemical stability[2] and increased biological reactivity to these analogues. Since neither functionalized ring system has been reported in the literature,[3,4] a new approach had to be devised that would produce useful quantities of **1** and **2**. In this paper is described a convenient and practical synthesis of these unusual bicyclic dipeptides using an intramolecular enolate epoxide cyclization reaction.



BICYCLOMYCIN



1



2

(±)-*N*-Carbobenzoxyhomoserine (**3**) is silylated (Me_2Bu^tSiCl, DMF, Et_3N, 0 °C) and condensed with *N*-*p*-methoxybenzylglycine ethyl ester (DCC, THF, 25 °C) to afford the dipeptide **5**. Without purification, **5** was directly subjected to hydrogenolysis (10% Pd/C, H_2, EtOH, 1 atm) to afford the piperazinedione **6** in 40% overall yield from **3** (Scheme I). Alkylation of the remaining amide nitrogen with *p*-methoxybenzyl chloride in DMF in the presence of NaH furnished the fully protected substrate **7** (79%).[5] Desilylation (HF–Py complex) furnished alcohol **8** (87%) that was oxidized to the aldehyde **9** (78%). Homologation of the aldehyde with dimethylsulfoxonium methylide afforded the epoxides **10** (1:1

†Fellow of the Alfred P. Sloan Foundation 1986–88. NIH Research Career Development Awardee 1984–89. Eli Lilly Grantee 1986–88.

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0022-3263/87/1952-4044$01.50/0