methoxybenzyl chloride (0.77 mL, 5.68 mmol) and anhydrous NaBr (2.9 g, 28.2 mmol) was stirred in 5 mL of DMF at room temperature for 2 h. The suspension was filtered, and the solid was washed with 3 mL of *p*-dioxane. The filtrate was subsequently transferred to a mixture of cephalothin (1.5 g, 3.79 mmol) and $NaHCO_3$ (0.35, 4.17 mmol), and the suspension was stirred at room temperature overnight. This mixture was diluted with a mixture of saturated $CaCl_2$ and ethyl acetate. The ethyl acetate fraction was washed twice more with saturated $CaCl_2$, water, saturated $NaHCO_3$, and water followed by drying over $MgSO_4$. The organic layer was subsequently evaporated to dryness in vacuo. The residue was crystallized from ethyl acetate at −20 °C to give 1.52 g of a white crystalline product: yield, 77% mp 144–146 °C; IR ($CHCl_3$) 1781, 1731, 1710, 1682, 1210 cm^{-1}; R_f 0.37 (3:1 benzene/ethyl acetate); ^1H NMR ($CDCl_3$) δ 2.03 (s, 3 H, acetoxymethyl), 3.33, 3.50 (2 d, 2 H, C-2, J = 18.5 Hz), 3.79 (s, 3 H, methoxy), 3.84 (s, 2 H, side-chain methylene), 4.79, 5.04 (2 d, 2 H, C-10, J = 13.4 Hz), 4.92 (d, 1 H, C-6, J = 4.8 Hz), 5.16, 5.20 (2 d, 2 H, benzylic, J = 11.8 Hz), 5.80 (m, 1 H, C-7), 6.27 (d, 1 H, NH, J = 9.1 Hz), 6.86 (d, 2 H, phenyl, J = 8.6 Hz), 6.97 (m, 2 H, thienyl), 7.25 (m, 1 H, thienyl), 7.30 (d, 2 H, phenyl, J = 8.6 Hz). Anal. ($C_{24}H_{24}N_2O_7S_2$) C, H, and N.

Acknowledgment. This work was supported by PHS Grant GM 29660. We also gratefully acknowledge the NIH (University of Chicago Cancer Grant CA 14599) and the Louis Block Fund for awards in support of the NMR facility used in this research.

Registry No. **6a**, 41625-53-0; **6b**, 52646-45-4; **6c** (isomer 1), 41095-78-7; **6c** (isomer 2), 41095-52-7; **6d**, 104949-45-3; **6e**, 19702-56-8; **6f**, 16234-22-3; **7a**, 105064-09-3; **7b**, 65480-09-3; **8a**, 105040-04-8; **8b**, 105040-05-9; **8c**, 105040-06-0; cephalothin, 153-61-7; *p*-nitrobenzyl bromide, 100-11-8; *p*-methoxybenzyl chloride, 824-94-2; benzyl bromide, 100-39-0; allyl iodide, 556-56-9; methyl iodide, 74-88-4; chloroacetone, 78-95-5; cefoxitin, 35607-66-0; cefuroxime, 55268-75-2.

Supplementary Material Available: Experimental details for the syntheses of compounds **6c–8c**, together with NMR, IR, and elemental analytical data for each compound (5 pages). Ordering information is given on any current masthead page.

Synthesis of Chiral Bis-Homoallylic Epoxides. A New Class of Lepidopteran Sex Attractants†,[1]

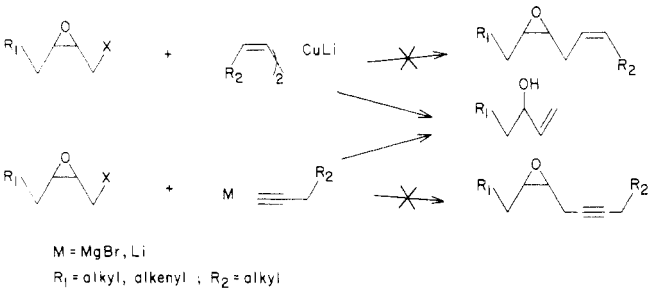
Jocelyn G. Millar* and Edward W. Underhill

Plant Biotechnology Institute, National Research Council, Saskatoon, Saskatchewan, Canada S7N 0W9

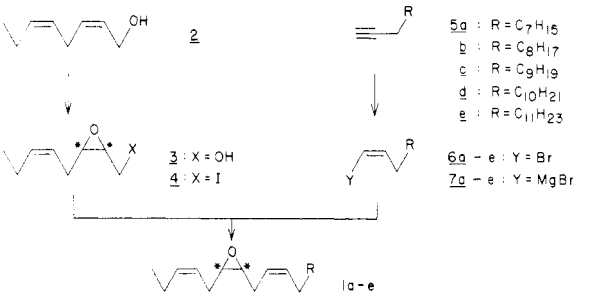
Received March 25, 1986

As part of an ongoing program to identify sex attractants for lepidopteran pests from the families Noctuidae and Geometridae, we required the enantiomers of a homologous series of (3*Z*,9*Z*)-*cis*-6,7-epoxyalka-3,9-dienes of chain lengths C_{18}–C_{22} (**1a–e**).[2] An efficient route to homoallylic epoxides such as **1** could utilize alkylation of a 1-halo 2,3-epoxide with a (*Z*)-alkenyl anion equivalent (Scheme I). A number of attempts at realizing this coupling were not successful, using standard alkylation conditions. In particular, addition of 1-halo or 1-tosyl *cis*-2,3-epoxide model compounds to a dialkenyllithium cuprate[3] in THF, ether, or THF/ether mixtures with varying proportions of HMPA and/or triethyl phosphite, at temperatures of −30 to +20 °C, was not successful. The major product from these reactions was invariably the allylic alcohol product from reductive elimination (Scheme I). In a similar fashion, addition of 1-iodo *cis*-2,3-epoxides to alkynyl-

Scheme I



Scheme II



lithium or alkynyl-Grignard reagents in THF/HMPA, with and without CuI catalysis, gave predominantly the allylic alcohol. We finally overcame this problem with the aid of a recent report by Nicolaou et al.,[4] who reported that inverse addition of vinylmagnesium bromide to preformed solutions of several 1-iodo 2,3-epoxides with a catalytic amount of cuprous iodide in THF/HMPA afforded good yields of the desired nucleophilic substitution products. Control of the reaction conditions was reported to be critical, as changes in the solvent and the order of addition of reagents gave high yields of the allylic alcohol products of reductive elimination instead. This report prompted us to try extending this reaction to substituted alkenyl-Grignard reagents. There were still two uncertainties: first, whether the chemoselection of the alkylation would be maintained with a substituted alkenyl anion, and, second, whether the *Z* stereochemistry of the alkenyl anion would be maintained under the reaction conditions. We have found that 1-iodo *cis*-2,3-epoxides are chemospecifically alkylated by THF solutions[5] of monosubstituted alkenyl-Grignard reagents under the reported conditions, with a minimum 93% retention of the (*Z*)-alkene geometry (in 12 trials).

With this key reaction in hand, we proceeded to the synthesis of the title compounds. An efficient route to one homologous series of diene epoxide enantiomers would use a common intermediate, to which a carbon chain of varying length could be appended. In addition, asymmetric epoxidation[6] of an appropriate allylic alcohol precursor such as **2** would conveniently provide access to either enantiomer. This reasoning led to a short and efficient route to the title compounds (Scheme II). Thus, allylic alcohol **2** was subjected to asymmetric epoxidation,[6] using (+)- or (−)-diisopropyl tartrate to form the chiral catalyst complex, giving epoxy alcohols (2*R*,3*S*)-**3** (75%) and (2*S*,3*R*)-**3**

† Issued as NRC No. 26109.

(1) First disclosed at the International Symposium on the Chemistry of Natural Products, June 23–26, 1985, Edmonton, Alberta.
(2) Wong, J. W.; Underhill, E. W.; MacKenzie, S. L.; Chisholm, M. D. *J. Chem. Ecol.* **1985**, *11*, 727.
(3) Alexakis, A.; Cahiez, G.; Normant, J. F. *Synthesis* **1979**, *826*. Gardette, M.; Alexakis, A.; Normant, J. F. *J. Chem. Ecol.* **1983**, *9*, 225.
(4) Nicolaou, K. C.; Duggan, M. E.; Ladduwahetty, T. *Tetrahedron Lett.* **1984**, *25*, 2069.
(5) Normant, H. *Adv. Org. Chem.* **1960**, *2*, 1.
(6) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.

0022-3263/86/1951-4726$01.50/0

(77%), each with an enantiomeric excess of greater than 88%. The alcohols **3** were converted to the epoxy iodides **4** (71, 77%), using triphenylphosphine/imidazole/iodine in ether/acetonitrile (3:1).[7] These iodides formed the common intermediates to which a variable-length chain could be attached.

The (*Z*)-alkenyl bromides required to make the Grignard reagents for the final coupling step were readily available from terminal acetylenes **5** by the one-pot sequence[8] of hydroboration with catecholborane, bromination of the resulting alkenylboranes, and stereoselective base-induced elimination of the elements of bromocatecholborane, giving the bromides **6** (71–90%), contaminated with 5% of other isomers.

The syntheses of **1a–e** were completed by dropwise addition of a THF solution of the appropriate (*Z*)-alkenylmagnesium bromide **7** (2 equiv) to a THF solution of the appropriate epoxy iodide enantiomer **4** (1 equiv), HMPA (4 equiv), and cuprous iodide (0.1 equiv), cooled to −23 °C. The bis-homoallylic epoxides **1** were obtained in 40–63% isolated yields, after a somewhat lengthly workup involving flash chromatography on silica gel, flash chromatography on silica gel impregnated with 10% silver nitrate to remove traces of geometric isomers, and Kugelrohr distillation to remove traces of chromatographic packing material, which otherwise seem to catalyze decomposition/polymerization of the products.[9]

In summary, the coupling reaction described provides a short and regiospecific route to homoallylic epoxides from readily available 2,3-epoxy alcohols. In particular, when used in conjunction with the asymmetric epoxidation sequence, the reaction allows ready access to the enantiomers of homoallylic epoxides, moieties that occur in the new class of lepidopteran sex attractants shown here, and in other important natural products such as arachidonic acid metabolites.[10]

Experimental Section

Glassware was oven-dried (120 °C) and cooled under nitrogen. All reactions were run under a positive pressure of nitrogen. THF was distilled from sodium benzophenone ketyl, methylene chloride was distilled from calcium hydride, and HMPA was distilled from barium oxide. Flash chromatography was performed with silica gel (230–400 mesh, Terochem Laboratories). Proton NMR spectra were recorded on a Bruker WM 360 instrument, operated at 360 MHz, or on a Varian EM390 instrument at 90 MHz. Infrared spectra were recorded with a Perkin-Elmer 237B instrument, using neat films on NaCl plates or chloroform solutions. Mass spectra (EI, 70 eV) were recorded with a Finnigan 4000E GC-MS instrument with an Incos 2300 data system. MS data are reported in the form *m/z* (relative intensity). Optical rotations were measured on a Perkin-Elmer 141 polarimeter, in a 1-dm cell. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbour, MI.

(2*R*,3*S*,5*Z*)-2,3-Epoxy-5-octen-1-ol ((2*R*,3*S*)-3) and (2*S*,3*R*)-3. Dry methylene chloride (400 mL) under nitrogen was cooled to −30 °C, and titanium isopropoxide (29.7 mL, 100 mmol) and (−)-diisopropyl tartrate (23.4 mL, 110 mmol; Aldrich) were added sequentially. The mixture was stirred 15 min at −30 °C, followed by dropwise addition of freshly distilled dienol **2** (12.6 g, 100 mmol; Terochem Laboratories), further stirring for 15 min, and dropwise addition of *tert*-butyl hydroperoxide (42.1 mL of 4.75 M in methylene chloride, 200 mmol). The resulting mixture was maintained at −29 °C for 65 h. The mixture was worked up by dropwise addition of aqueous tartaric acid (10%, 250 mL) with vigorous mechanical stirring, maintaining the temperature below −20 °C. The resulting thick slurry was stirred a further 30 min at −20 °C, then warmed slowly to 20 °C, and stirred until the aqueous layer became clear (approximately 1 h). The layers were separated and the aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined organic extracts were cooled to 0 °C, and aqueous sodium sulfite (125 mL of 1 M, 125 mmol) was added dropwise over 2 h. The mixture was then allowed to warm to 20 °C and stirred until acidified starch iodide paper gave a negative peroxide test (8 h). The layers were separated and the organic layer was washed with brine (1 × 100 mL), dried (Na_2SO_4), concentrated, and fractionally distilled, giving (2*R*,3*S*)-**3** (10.93 g, 77%): bp 60–61°C (0.08 torr); $[\alpha]^{21}_D$ +6.5° (neat). The enantiomeric excess of (2*R*,3*S*)-**3** was determined by esterification with (2*S*)-acetoxypropionyl chloride, and capillary GC of the diastereomeric mixture on a DB-210 column (0.256 mm × 30 m) at 150 °C. Base-line separation was obtained, giving an enantiomeric excess of 88.2%: ^{1}H NMR ($CDCl_3$) δ 5.53 (m, 1 H, H-6), 5.36 (m, 1 H, H-5), 3.84 (ddd, 1 H, *J* = 12.0, 7.0, 4.4 Hz, H-1), 3.72 (ddd, 1 H, *J* = 12.0, 6.6, 5.4 Hz, H-1), 3.15 (ddd, 1 H, *J* = 6.6, 4.4, 4.3 Hz, H-2), 3.05 (ddd, 1 H, *J* = 6.6, 6.5, 4.3 Hz, H-3), 2.43 (m, 1 H, H-4), 2.22 (m, 1 H, H-4), 2.04 (m, 2 H, H-7), 1.59 (dd, 1 H, *J* = 7.0, 5.4 Hz, OH), 0.96 (t, 3 H, *J* = 7.5 Hz, H-8); IR (neat) λ_{max} 3600–3200 (br s), 3020 (m), 2975 (s), 2940 (m), 2880 (m), 1040 (br s) cm^{-1}; MS, 125 (M − 17, 0.5), 111 (35.4), 95 (11.6), 93 (11.2), 83 (23.2), 81 (38.4), 69 (26.5), 68 (19.7), 67 (62.0), 57 (47.0), 55 (100), 54 (22.2), 53 (24.6), 43 (64.3).

(2*S*,3*R*)-**3** was prepared in similar fashion, using (+)-diisopropyl tartrate in the asymmetric epoxidation mixture. The enantiomeric excess determined as described above, was 88.3%: $[\alpha]^{21}_D$ −6.4° (neat).

(2*S*,3*S*,5*Z*)-1-Iodo-2,3-epoxyoct-5-ene ((2*S*,3*S*)-4) and (2*R*,3*R*)-4. Triphenylphosphine (20.44 g, 78 mmol) and imidazole (5.3 g, 78 mmol) were dissolved in ether/acetonitrile (3:1, 300 mL). The mixture was cooled in an ice bath, and iodine (19.81 g, 78 mmol) was added in four portions with vigorous stirring over 20 min. The resulting slurry was warmed to 20 °C and then cooled to 0 °C again, and (2*R*,3*S*)-**3** (10.13 g, 71 mmol) was added dropwise over 15 min. The mixture was warmed to 20 °C and stirred 1 h and then cooled to 0 °C, and pentane (300 mL) was added. The top layer was decanted off, and 5% aqueous sodium bicarbonate (200 mL) was added to the bottom layer. The aqueous mixture was extracted with pentane (2 × 50 mL). The combined pentane extracts were concentrated, and the residue was triturated with pentane (2 × 100 mL). The combined pentane solutions were concentrated and flash chromatographed (4 cm i.d. × 25 cm, pentane/ether, 19:1), giving (2*S*,3*S*)-**4** (12.7 g, 71%): $[\alpha]^{27}_D$ +80.6° (neat). The iodide discolored in light and air and was stored in brown glass vials at −30 °C under nitrogen: ^{1}H NMR ($CDCl_3$) δ 5.54 (dtt, 1 H, *J* = 10.8, 7.3, 1.5 Hz, H-6), 5.41 (dtt, 1 H, *J* = 10.8, 7.3, 1.5 Hz, H-5), 3.31 (m, 2 H, H-1), 3.04 (m, 2 H, H-2, H-3), 2.28 (m, 2 H, H-4), 2.06 (br dq, 2 H, *J* = 7.5, 7.3 Hz, H-7), 0.97 (t, 3 H, *J* = 7.5 Hz, H-8); IR (neat) λ_{max} 3020 (m), 2970 (s), 2940 (m), 2880 (m) cm^{-1}; MS, 252 (M$^+$, 0.64), 183 (18.9), 155 (16.7), 81 (32.5), 79 (17.9), 69 (45.3), 67 (24.1), 57 (55.4), 55 (100), 53 (19.8), 43 (22.9).

(2*R*,3*R*)-**4** was synthesized in a similar fashion in 85% yield, $[\alpha]^{25.5}_D$ −79.0°.

(1*Z*)-1-Bromo-1-alkenes 6a–e. The following procedure describes the preparation of **6a**: **6b–e** were prepared in identical fashion. Catecholborane (8.0 mL, 72 mmol; Aldrich) was added dropwise with stirring to 1-decyne (**5a**) (8.28 g, 60 mmol) in a 500-mL three-necked flask under argon. When the initial exothermic reaction subsided, the mixture was warmed and stirred 3 h at 70 °C. The mixture was cooled to 20 °C and methylene chloride (75 mL) was added. The solution was cooled to −20 °C, and bromine (23.0 g, 144 mmol) was added dropwise, followed by warming and stirring at 0 °C for 1 h. The mixture was then

(7) Corey, E. J.; Pyne, S. G.; Su, W. *Tetrahedron Lett.* **1983**, *24*, 4883.
(8) Brown, H. C. *Organic Synthesis via Boranes*; Wiley: New York, 1975; pp 105–107.
(9) Although there was no reason to suppose that any racemization had occurred between epoxy alcohol **3** and the final products **1**, attempts were made to determine the chiral purity of epoxides **1** directly. Experiments with chiral NMR shift reagents, both with the epoxides **1** and with the saturated epoxides from catalytic reduction of **1**, were not successful. In addition, diastereomeric derivatives of the diene alcohols formed by $LiAlH_4$ reduction of **1** followed by derivatization as described for **2** were chromatographically inseparable on several capillary GC columns. Similarly, catalytic reduction of these derivatives gave saturated compounds that were also chromatographically inseparable.
(10) For example: Oliw, E. H.; Guengerich, F. P.; Oates, J. A. *J. Biol. Chem.* **1982**, *257*, 3771. Chacos, N.; Falck, J. R.; Wixtrom, C.; Capdevila *J. Biochem. Biophys. Res. Commun.* **1982**, *104*, 916.

cooled to −20 °C again, and NaOMe (290 mmol, freshly prepared) in MeOH (150 mL) was added dropwise with vigorous stirring, maintaining the temperature below −15 °C. The mixture was allowed to warm to 20 °C, and water (100 mL) was added. The layers were separated, and the aqueous phase was extracted with methylene chloride (2 × 25 mL). The combined organic extracts were dried (Na_2SO_4), concentrated, and distilled. After a considerable low-boiling forerun, bromodecene **6a** (9.35 g, 71%), bp 56–57 °C (0.8 torr), was obtained, contaminated with 5% of two isomeric products: ^{1}H NMR ($CDCl_3$) δ 6.11 (dt, 1 H, J = 6.9, 1.3 Hz, H-1), 6.06 (dt, 1 H, J = 6.9, 6.9 Hz, H-2), 2.17 (tdd, 2 H, J = 6.9, 6.9, 1.3 Hz, H-3), 1.40 (m, 2 H, H-4), 1.32–1.20 (m, 10 H, H-5–H-9), 0.86 (t, 3 H, J = 6.8 Hz, H-10); IR (neat) λ_{max} 3090 (w), 2960 (m), 2930 (s), 2860 (s), 1625 (m), 1460 (m, br) cm^{-1}; MS, 218, 220 (M^+, 1.9), 162, 164 (1.8), 148, 150 (4.4), 135, 137 (2.3), 119, 121 (7.7), 97 (32), 83 (49), 69 (45), 57 (100), 55 (93), 43 (37). Yields and boiling points of **6b–e**: **6b** (77%), bp 45–50 °C (0.05 torr); **6c** (68%), bp 72–75 °C (0.1 torr); **6d** (90%), bp 86–88 °C (0.3 torr); **6e** (80%), bp 87–88 °C (0.07 torr). NMR and IR spectra of **6b–e** were analogous to those of **6a**. Mass spectra were characterized by pairs of molecular ion peaks (1–2%) and were otherwise similar to the mass spectrum of **6a**, with the exception of an additional fragment at m/z 111 (11–31%).

(3*Z*,9*Z*,6*S*,7*R*)-6,7-Epoxy-3,9-alkadienes ((6*S*,7*R*)-1a–e) and (6*R*,7*S*)-1a–e. The following procedure describes the synthesis of (6*S*,7*R*)-**1a**. The syntheses of (6*S*,7*R*)-**1b–e** were performed under identical conditions, using the appropriate (*Z*)-alkenyl bromides **6**. The syntheses of (6*R*,7*S*)-**1a–e** were carried out in similar fashion, using the other enantiomer of iodide **4**.

A solution of (*Z*)-1-decenylmagnesium bromide (**7a**) was prepared by slow addition of a THF solution (15 mL) of (*Z*)-1-bromo-1-decene (**6a**) (3.50 g, 16 mmol) to Mg turnings (1.556 g, 64 mmol) in THF, at 10–30 °C. The solution of alkenyl-Grignard was then added dropwise by syringe to a cooled (−23 °C) preformed solution of (2*R*,3*R*)-epoxy iodide **4** (2.016 g, 8 mmol), cuprous iodide (152 mg, 0.8 mmol), and HMPA (5.9 mL, 32 mmol) in THF (20 mL), maintaining the temperature below −20 °C. The resulting mixture was stirred 30 min at −23 °C and then quenched by addition of cold aqueous saturated ammonium chloride solution. The mixture was extracted with ether (1 × 50 mL, 2 × 25 mL), and the combined ether extracts were washed with water and brine (25 mL each), dried (Na_2SO_4), and concentrated. The crude product was then purified by flash chromatography on silica gel (4 cm i.d. × 20 cm, 1.5% ether in hexane), followed by flash chromatography on silica gel impregnated with silver nitrate (10% w/w; 3 cm i.d. × 20 cm, stepwise gradients of 10, 15, and 20% ether in hexane). Final purification was accomplished by Kugelruhr distillation (0.1 torr, oven temperature 150 °C), giving (6*S*,7*R*)-**1a** (1.05 g, 50%): $[\alpha]^{23}_{365}$ − 1.1 (*c* 6.47, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 5.52 (dtt, 2 H, J = 10.8, 7.2, 1.5 Hz, H-3, H-10), 5.40 (m, 2 H, H-4, H-9), 2.92 (m, 2 H, H-6, H-7), 2.38 (m, 2 H, H-5, H-8), 2.18 (m, 2 H, H-5, H-8), 2.03 (m, 4 H, H-2, H-11), 1.4–1.1 (m, 12 H, H-12–H-17), 0.95 (t, 3 H, J = 7.5 Hz, H-1), 0.84 (t, 3 H, J = 7.5 Hz, H-18); IR (neat) λ_{max} 3020 (w), 2970 (m), 2930 (s), 2860 (m) cm^{-1}; MS, 264 (M^+, 0.5), 235 (1.2), 195 (3.1), 181 (1.4), 177 (1.6), 165 (1.6), 151 (3.1), 137 (4.5), 121 (8.5), 111 (27.5), 109 (20.7), 95 (42.3), 83 (77.7), 67 (98.3), 55 (100), 43 (64.2).

The compounds (6*S*,7*R*)-**1b–e** and the enantiomeric series (6*R*,7*S*)-**1a–e** were synthesized by the same procedure and on the same scale, using the appropriate iodide enantiomers and the appropriate alkenylmagnesium bromides. 6*S*,7*R* series: **1b** (63%), $[\alpha]^{23}_{365}$ −1.0° (*c* 8.20, CH_2Cl_2); **1c** (49%), $[\alpha]^{21}_{365}$ − 1.1° (*c* 7.26, CH_2Cl_2); **1d** (42%), $[\alpha]^{24}_{365}$ − 1.0° (*c* 7.40, CH_2Cl_2); **1e** (59%) $[\alpha]^{24}_{365}$ −1.1° (*c* 6.22, CH_2Cl_2). 6*R*,7*S* series: **1a** (53%), $[\alpha]^{23}_{365}$ +1.1° (*c* 5.69, CH_2Cl_2); **1b** (51%), $[\alpha]^{23}_{365}$ +1.2° (*c* 5.68, CH_2Cl_2); **1c** (54%), $[\alpha]^{21}_{365}$ +1.1 (*c* 5.33, CH_2Cl_2); **1d** (40%), $[\alpha]^{24}_{365}$ +1.0° (*c* 5.11, CH_2Cl_2); **1e** (59%), $[\alpha]^{23}_{365}$ +1.2° (*c* 6.10, CH_2Cl_2).

The NMR and IR spectra of (6*S*,7*R*)-**1b–e** and (6*R*,7*S*)-**1a–e** were entirely analogous to those of (6*S*,7*R*)-**1a** reported above. The mass spectra of the series were characterized by ions corresponding to M, M − 29, M − 69, M − 83, M − 87, m/z 111, and clusters of peaks centered at m/z 165, 151, 137, 121, 109, 95, 83, 67, 55, and 43, at intensities similar to those of the corresponding ions in the spectrum of (6*S*,7*R*)-**1a**.

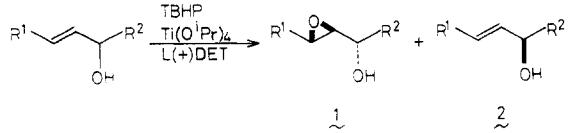
Anal. Calcd for (6*R*,7*S*)-**1e**, $C_{22}H_{40}O$: C, 82.43; H, 12.58. Found: C, 82.52; H, 12.65.

Communications

Synthesis of Optically Active β,γ-Epoxy Alcohols and Secondary Allylic Alcohols via Diastereoselective Addition of α-Trimethylsilyl-α,β-epoxy Aldehydes with Organometallic Compounds

Summary: Optically active α-trimethylsilyl-α,β-epoxy aldehydes **3** react with various Grignard reagents or organolithium compounds highly stereoselectively to give erythro adducts **4**, which can be readily converted into β,γ-epoxy secondary alcohols **1** or secondary allylic alcohols **2**.

Sir: Kinetic resolution of racemic allylic alcohols by the Sharpless process used to prepare optically active β,γ-epoxy alcohols **1** or secondary allylic alcohols **2** is highly effective and reliable (eq 1).[1,2]

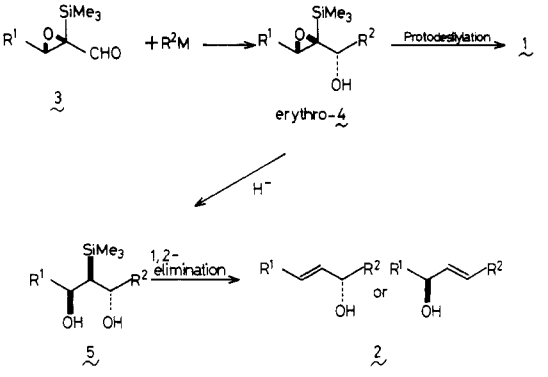


(1)

1 **2**

(1) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237.

Scheme I



3 **5**

However, kinetic resolution suffers from the disadvantage that at least half of the starting material is lost. We wish to report a new method for preparation of **1** and **2**

(2) Recent other method for preparation of optically active secondary allylic alcohols: (a) Noyori, R. *Pure Appl. Chem.* **1981**, *53*, 2315. (b) Yamamoto, H.; Fujiwara, J.; Fukutani, Y.; Hasegawa, M.; Maruoka, K. *J. Am. Chem. Soc.* **1981**, *53*, 2315. (c) For related work, see: Kitano, Y.; Matsumoto, T.; Sato, F. *J. Chem. Soc., Chem. Commun.*, in press.

0022-3263/86/1951-4728$01.50/0