signals of cystine were observed in place of signals of cysteine hydrochloride, and the signals of **6a** had disappeared. Cysteine hydrochloride: ^{1}H NMR δ 3.65 (d, J = 5.0 Hz, 2 H), 4.84 (t, J = 5.0 Hz, 1 H). Cystine hydrochloride: ^{1}H NMR δ 3.81 (d ABq, A-part, J = 7.5, 16.0 Hz, 1 H), 3.93 (d ABq, B-part, J = 5.0, 16.0 Hz, 1 H), 5.00 (dd, J = 5.0, 7.5 Hz, 1 H). The scale-up experiment also gave cystine quantitatively as a colorless powder.

UV Measurements of the Exchange Reaction between 6a and Cysteine Hydrochloride. A solution of cysteine hydrochloride in a phosphate buffer solution, pH 6.8 (0.05 mmol/L, 2.00 mL), was shaken in a cell with a solution of **6a** (0.05 mmol/L, 2.00 mL) in the same buffer solution at 20 °C, and the mixture was quenched immediately with a phosphate buffer solution (pH 2.0). The UV spectrum of the resulting solution was measured in a rapid-scan mode with a Hitachi 320 UV spectrometer. The absorption of **6a** (end absorption) disappeared, and the absorption of NMTT (λ_{max} 235 nm) was observed quantitatively.

Thiol–Disulfide Exchange Reaction between 7 and 6b. To a solution of disulfide **6b** (355 mg, 1 mmol) in 5 mL of THF was added a solution of thiol **7** (241 mg, 1 mmol) in 2 mL of THF, and the mixture was partitioned between AcOEt and 5% aqueous $NaHCO_3$. The organic solution was washed with H_2O, dried, and concentrated in vacuo. Chromatographic purification (SiO_2 30 g, eluted with CH_2Cl_2–AcOEt (10%)) gave 457 mg (95.0%) of disulfide **8** as colorless flakes: mp 122–123 °C; ^{1}H NMR ($CDCl_3$) δ 2.76 (t, J = 6.0 Hz, 4 H), 3.46 (q, J = 6.0 Hz, 4 H), 3.78 (s, 6 H), 5.02 (s, 4 H), 5.25 (br s, 2 H), 6.75–7.40 (m, 8 H). Anal. Calcd for $C_{22}H_{28}N_2O_6S_2$: C, 54.97; H, 5.88; N, 5.83; S, 13.34. Found: C, 54.99; H, 5.80; N, 5.91; S, 13.37.

Thiol–Disulfide Exchange Reaction between Dithiothreitol (DTT) and 6b. To a solution of **6b** (105 mg, 0.296 mmol) in 5 mL of THF was added 22.8 mg (0.296 mmol × 0.5) of dithiothreitol at rt, and the reaction mixture was partitioned between AcOEt and 5% aqueous $NaHCO_3$. The organic solution was washed with H_2O, dried, and concentrated in vacuo. Crystallization of the residue from ether gave 90.5 mg (96.7%) of **9** as colorless plates: mp 102–103 °C; ^{1}H NMR ($CDCl_3$) δ 2.83 (t, J = 6.2 Hz, 4 H), 2.93 (m, 6 H), 3.52 (q, J = 6.2 Hz, 4 H), 3.81 (s, 6 H), 3.91 (td, J = 6.2, 7.0 Hz, 2 H), 5.03 (s, 4 H), 5.17 (t, J = 6.2 Hz, 2 H), 6.84–6.95 (m, 4 H), 7.20–7.35 (m, 4 H); IR (Nujol) 3350, 1683, 1536, 1031 cm^{-1}. Anal. Calcd for $C_{26}H_{36}N_2O_8S_4$: C, 49.35; H, 5.73; N, 4.43; S, 20.26. Found: C, 49.15; H, 5.72; N, 4.42; S, 20.16.

Enzymatic Resolution of 2-Substituted Oxiranemethanols, a Class of Synthetically Useful Building Blocks Bearing a Chiral Quaternary Center†

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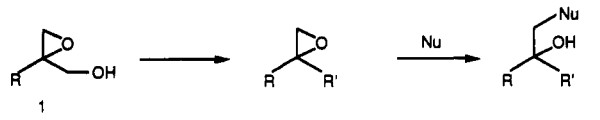
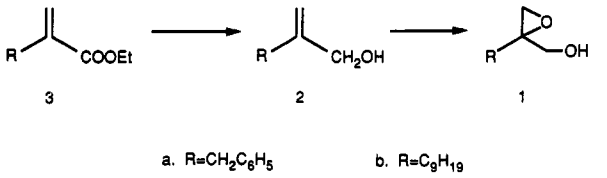
2-Substituted oxiranemethanols **1** can be considered synthetically useful building blocks bearing a quaternary carbon constituted by an oxirane ring. The fact that epoxides are versatile and important intermediates in organic synthesis is well-documented.[1] In the case of 2-substituted oxiranemethanols, the heterocyclic ring can be opened by a variety of reagents, so that synthetic applications can be summarized in Scheme I. Chiral epoxides can be prepared either by the Sharpless asymmetric epoxidation of allylic alcohols[2] or by enzymatic resolution of epoxy esters.[3] We wish to report here that enantiomerically pure oxiranemethanols of type **1** can be obtained by the enzymatic transesterification procedure developed by Wong[4] that we have successfully applied to the resolution of a few 2-methylalkanols.[5] *Pseudomonas fluorescens* lipase (PFL, Fluka, Switzerland) was used as the biocatalyst in an organic solvent, and vinyl acetate was the acyl donor. A few examples of preparation of chiral **1** are already available by the Sharpless asymmetric epoxidation of the proper allylic alcohol **2**.[6] A general access to these methylene alcohols is still lacking,[7] and for the purpose of our work we relied upon a recently described preparation of α-alkylated acrylic esters of type **3**.[8]

These esters could be reduced to the corresponding allylic alcohols **2** with diisobutylaluminum hydride (2 equiv in THF, −30 °C) and further epoxidized to oxiranemethanols by the vanadium acetylacetonate/*tert*-butyl

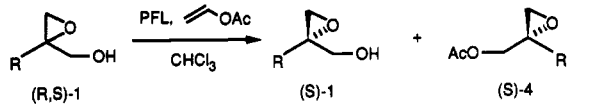
Scheme I



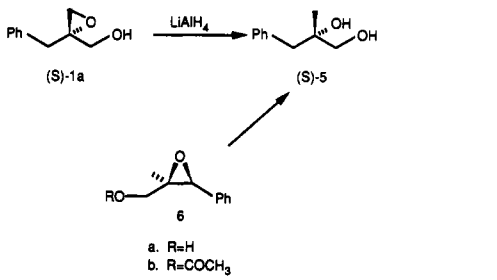
Scheme II



Scheme III



Scheme IV



†This work is dedicated to the memory of Professor Alberto Fiecchi, deceased on January 24, 1991.

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hydroperoxide procedure[9] (Scheme II). Yields of the substrates **1a** and **1b** for the enzymatic reaction were 70% starting from the ester **3**. As a model, we examined the PFL-catalyzed transacetylation of the epoxide **1a**, and at 60% conversion to the acetate **4a**, we obtained the (−)-alcohol **1a**, $[\alpha]_D$ −39°.[10] The enantiomeric excess was determined by the 500-MHz ^1H NMR spectrum of its ester with (*S*)-MTPA chloride[11] and established as >98%.[12] At 40% conversion to the corresponding acetate, compound (+)-**4a** was obtained, $[\alpha]_D$ +25° (Scheme III). Its optical purity was >98%, as established by comparison with the (−)-acetate **4a** prepared by acetylation of previously prepared (−)-alcohol **1a**.[13] Since the configurations of **1a** and **4a** were unknown, we subjected the allylic alcohol **2a** to the Sharpless epoxidation with L-tartrate as chiral auxiliary. By this procedure the (*S*)-(−)-alcohol **1a** was obtained (60% yield, $[\alpha]_D$ −26°, 80% ee), thus confirming that the chiral alcohol (−)-**1a** enzymatically prepared was *S*. Thus, the acetate **4a** enzymatically prepared was the ester of the enantiomeric alcohol (*R*)-(+)-**1a**, namely the compound (*S*)-(+)-**4a**.[14]

$LiAlH_4$ reduction of the enzymatically prepared (*S*)-(−)-**1a** (>98% ee) afforded the corresponding (*S*)-(−)-diol **5** (α_D −7.3°). The same diol could, in principle, be obtained from the epoxy alcohol **6a** of *R* configuration at the quaternary center[15] (Scheme IV). It was therefore interesting to attempt the preparation of this compound in a stereoselective way by the PFL resolution of the racemic mixture of the epoxy alcohol **6a**.[16]

The transacetylation reaction proceeded fast, since after 3 h of incubation as for racemic **1a** the reaction was stopped when 20% of alcohol **6a** and 80% of acetate **6b** were present in the mixture. The (+)-epoxy alcohol **6a** was obtained (16%), and its $LiAlH_4$ reduction afforded the (*S*)-(−)-diol **5** ($[\alpha]_D$ −1.5°, corresponding to 20% ee). Thus, compared to the oxiranemethanol **1a**, the PFL resolution of the more hindered epoxy alcohol **6a** was much less enantioselective. The substrate specificity of the PFL-catalyzed irreversible transesterification was confirmed by the observation that 3-methyl-3-oxetanemethanol **7** could not be acetylated after 24 h of incubation in the usual conditions.

7

The same enzymatic procedure, instead, applies successfully to the preparation of (*S*)- and (*R*)-2-nonyloxiranemethanol (**1b**), a valuable chiral intermediate for the synthesis of the antibiotic malyngolide and related compounds.[17] Should the stereochemical outcome apply also to the resolution of **1b**, we could prepare the (*S*)-alcohol **1b** and the corresponding isomeric acetate **4b** from (*R*,*S*)-**1b**. In fact, according to the established experimental protocol,[18] we subjected (*R*,*S*)-**1b** to the enzymatic transesterification. We were able to prepare (*S*)-(−)-**1b** and (*S*)-(+)-**4b** in 35–38% yields and 96% ee, as established by comparison of optical rotations[19] and for (*S*)-**1b** by the 500-MHz ^1H NMR spectrum of its MTPA ester.[20]

In conclusion, we have shown that the PFL-catalyzed transesterification of 2-substituted oxiranemethanols can constitute a valid alternative to the Sharpless methodology for the preparation of both enantiomers of these important chiral synthons. Further work is in progress in order to define the general stereochemical outcome as well as other synthetic applications of these valuable building blocks.

Experimental Section

Esters 3a and 3b. The preparation of compound **3a** was as described in ref 8, and its properties were in full agreement with structures and literature data.[8] For the ester **3b**, the intermediate ethyl 2-diethylphosphonoundecanoate was prepared from *n*-nonyl bromide and triethyl phosphonoacetate in the conditions described[8] (14 days, 70% yield). The ester **3b** was prepared in accord to the described experimental procedure (66% yield): bp 190 °C (14 mmHg); ^1H NMR (60 MHz, $CDCl_3$) δ 5.6 (s, 1 H, CH=), 6.25 (s, 1 H, CH=).

Alcohols 2a and 2b. These compounds were prepared from esters **3** with 2 equiv of diisobutyl aluminum hydride in THF at −30 °C (3 h, 70%). Alcohol **2a**: ^1H NMR (60 MHz, $CDCl_3$) δ 1.90 (m, 1 H, exch with ^2H_2O), 2.45 (s, 2 H, CH_2Ph), 4.10 (s, 2 H, CH_2OH), 5.00 (s, 1 H, CH=), 5.20 (s, 1 H, CH=), 7.25–7.45 (m, 5 H, aromatic). A sample distilled at 1 mmHg (210 °C) gave the following analysis. Anal. Calcd for $C_{10}H_{12}O$: C, 81.08; H, 8.11. Found: C, 81.19; H, 8.20. The alcohol **2b** had chemicophysical properties as described in ref 17.

(*R*,*S*)-Epoxy Alcohols 1a and 1b. The epoxidation was performed using the method described in ref 9. A 1 mmol portion of **1a** or **1b** was reacted with vanadium acetylacetonate (0.005 mmol) and *tert*-butyl hydroperoxide (1.2 mmol) in benzene (24 h). Yields after workup were 85% for **1a** and 82% for **1b**. **(*R*,*S*)-1a**: ^1H NMR (60 MHz, $CDCl_3$) δ 2.55–3.10 (m, 4 H, CH_2O and CH_2Ph), 3.20–4.60 (m, 1 H, exch with ^2H_2O), 4.62 (d, 2 H, CH_2OH, J = 2 Hz), 7.20–7.50 (m, 5 H, aromatic). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.17; H, 7.31. Found: C, 73.19; H, 7.37. The epoxy alcohol **1b** had chemicophysical properties as described in ref 17.

Enzymatic Transacetylation of (*R*,*S*)-Epoxy Alcohol 1a. To a solution of (*R*,*S*)-**1a** (1.5 g, 9.15 mmol) in chloroform (18 mL) were added vinyl acetate (3.4 mL, 36.8 mmol) and PFL (Fluka, Switzerland, 0.193 g, 31.5 U/mg). The suspension was kept at 30 °C for 3 or 6 h for 40% and 60% conversion to acetate, respectively. The enzyme was removed by filtration, and a mixture (2 g) of (*S*)-(−)-epoxy alcohol **1a** and the corresponding (*S*)-(+)-acetate **4a** was obtained after evaporation of the solvent. Purification on silica gel column chromatography afforded the

(9) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6135.

(10) All measurements of optical rotations are referred to *c* 2.5 in dichloromethane.

(11) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

(12) For the quantitative determination of the *R*/*S* ratio in the MTPA ester prepared from (*R*,*S*)-**1a** the signals corresponding to the C-2 methylene hydrogens were four doublets centered at 2.647, 2.667, 2.719, and 2.750 ppm, respectively. In the derivative prepared from enzymatic (*S*)-(−)-**1a**, only two doublets centered at 2.644 and 2.747 ppm were detectable.

(13) From >98% optically pure (−)-alcohol **1a**, $[\alpha]_D$ −39°, the corresponding (−)-acetate **4a** was prepared ($[\alpha]_D$ −25°).

(14) Due to the relative priorities of the groups, the acetates **4a** and **4b** formed by PFL catalysis are the esters of the (*R*)-alcohols **1a** and **1b**, but have the *S* configuration.

(15) The diastereomer depicted in Scheme IV is chosen arbitrarily. The configuration of the other chiral carbon is of no relevance for our purpose, since it is going to be destroyed during the reduction of **6a** to **5**.

(16) The mixture of diastereomers corresponding to compound **6a** was prepared in overall 72% yields from commercially available α-methyl cinnamic acid, esterification (EtOH, H_2SO_4), diisobutylaluminum hydride reduction (2 equiv in THF, −30 °C, 2 h) and epoxidation by vanadium acetylacetonate and *tert*-butyl hydroperoxide (24 h). ^1H NMR of **6a**: 1.2 (s, 3 H, CH_3), 2.6 (s, 1 H, exch), 3.95 (s, 2 H, CH_2OH), 4.35 (s, 1 H, CHO), 7.35–7.65 (aromatic).

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(18) The experimental procedure was essentially as described in ref 5b.

(19) The enzymatically prepared (*S*)-(−)-epoxy alcohol **1b** (96% ee) showed $[\alpha]_D$ −12.6° (*c* 2.5 in CH_2Cl_2) (lit.[17] −11.9° (*c* 13.4 in $CHCl_3$, >96% ee)) and the (*S*)-(+)-acetate **4b** had the optical rotation +5.9° (96% ee).

(20) From the 500-MHz ^1H NMR spectrum of its ester with (*S*)-MTPA chloride. In the diastereomeric derivative prepared from (*R*,*S*)-**1b** the signals corresponding to the C-1 methylene hydrogens were four doublets centered at 4.158, 4.253, 4.463, and 4.515 ppm. In the MTPA ester from **1b** prepared by the enzyme-catalyzed reaction, the two couples of doublets at 4.253 and 4.463 and at 4.158 and 4.515 ppm were in the ratio 98:2.

(*S*)-acetate **4a** and the (*S*)-alcohol **1a** (hexane/ethyl acetate = 9/1 and 8/2) with a ratio depending on the incubation time.

a. At 60% conversion, (*S*)-(−)-**1a** (0.51 g, 34%) was obtained; $[\alpha]_D$ −39° (>98% ee). The 60-MHz NMR spectrum was identical with the one previously reported for (*R,S*)-**1a**, and a correct elemental analysis was found.

b. At 40% conversion, the (*S*)-(+)-acetate **4a** (0.6 g, 32%) was isolated; $[\alpha]_D$ +25° (>98% ee). The chemicophysical data were in agreement with the structure.

Enzymatic Transacetylation of (*R,S*)-Epoxy Alcohol 1b. The experimental procedure was as for **1a**. Starting from (*R,S*)-**1b** (1.83 g, 9.15 mmol), the reaction reached 60% conversion to the acetate **4b** in 2 h and, after purification, (*S*)-(−)-**1b** (0.658 g, 36%) was obtained; $[\alpha]_D$ −12.6° (96% ee). When the reaction was carried out on the same amount of (*R,S*)-**1b** and at 40% conversion (1 h), the (*S*)-(+)-acetate **4b** (0.84 g, 38%) was isolated; $[\alpha]_D$ +5.9° (96% ee). The chemicophysical properties of compound **1b** were in agreement with the literature data (ref 17), and for the acetate **4b** the properties were in accord to the structure.

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Registry No. (±)-**1a**, 135107-04-9; (5)-**1a**, 135214-52-7; (±)-**1b**, 135214-51-6; (*s*)-**1b**, 103680-90-6; **2a**, 30457-89-7; **2b**, 103680-89-3; **3a**, 20593-63-9; **3b**, 84515-42-4; (*s*)-**4a**, 135107-05-0; (*s*)-**4b**, 135107-06-1; PFL, 9001-62-1; vanadium acetylacetonate, 13476-99-8; vinyl acetate, 108-05-4.

Divergent Response of a Hindered Cyclopropene to Strong Oxidizing Agents

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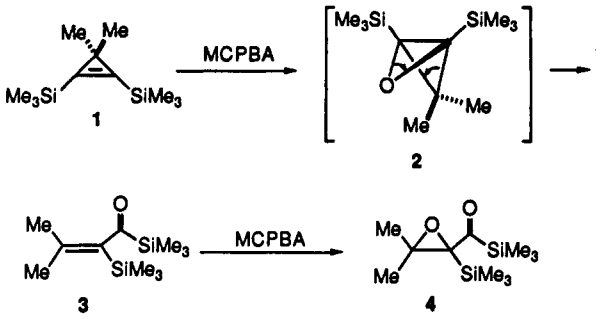
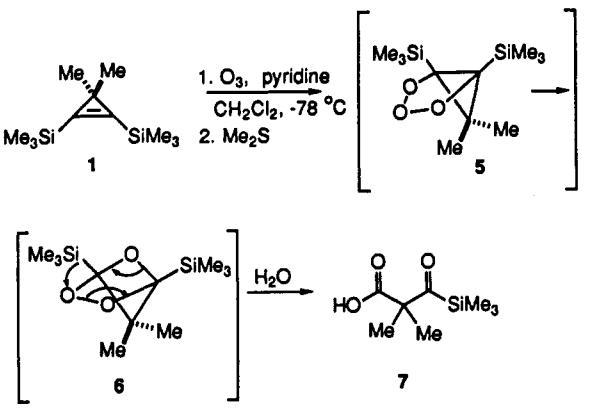
The inability to produce oxabicyclobutanes by direct epoxidation of a cyclopropene has been recognized for some time.[2] No member of this structurally interesting class of compounds has yet been characterized, presumably due to the substantial structural strain present in this highly condensed heterocyclic framework and the existence of a facile isomerization pathway under the conditions customarily employed. With the recent advent of dimethyldioxirane[3] and its trifluoromethyl analogue[4] on the chemical scene,[5] the combination of high reactivity, neutral pH, and ease of workup offered by these reagents suggested that they be examined for the possible elaboration of this extremely sensitive class of compounds.

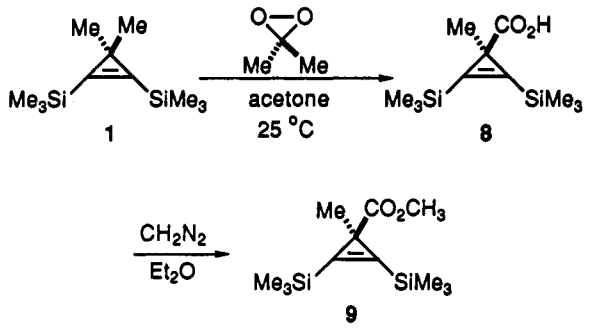
Scheme I



Scheme II



Scheme III



The stability of **1** and the beneficial steric shielding offered by its substitution prompted its selection for initial study.[6] This paper records the entirely different response exhibited by **1** toward *m*-chloroperbenzoic acid (MCPBA), ozone, and dimethyldioxirane (DMD).

The oxidation of **1** with MCPBA was carried out under several sets of conditions. Invariably, the major products were the α,β-unsaturated acylsilane **3** and its epoxide **4** (Scheme I). The oxidation was observed to proceed sluggishly, a reasonable rate materializing only when the reaction was conducted near room temperature. In accord with previous reports,[2] the appearance of **3** and **4** is considered to stem from transient formation of oxabicyclobutane **2** with ensuing electronic reorganization as shown.

Hindered alkenes often react with ozone to produce the epoxide rather than the expected products of ozonolysis.[7]

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