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Asymmetric Epoxidation of Chiral Allylic Alcohols

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Abstract: Two series of chiral allylic alcohols, derived from α,β-unsaturated cyanohydrins, were subjected to asymmetric epoxidation under a variety of conditions. Both achiral (organic peracid, metal-catalyzed peroxide) and chiral (Sharpless titanium-tartrate system) oxidants were applied. Several *threo* and all theoretically possible *erythro* epoxides were isolated in enantiomerically and diastereomerically pure form. Copyright © 1996 Elsevier Science Ltd

Introduction

In recent years research in our group has been focused on the synthesis and application of chiral cyanohydrins[1]. These cyanohydrins are prepared with the aid of the enzyme (R)-oxynitrilase as present in almonds (E.C. 4.1.2.10), and generally possess the (*R*)-configuration. A number of cyanohydrins of different structural types are now readily accessible in enantiomerically pure form, and transformations of the nitrile function, with preservation of enantiomeric purity, have been extensively described by our group[1] and by others[2]. Several products that can be obtained from cyanohydrins are promising chiral building blocks.

Recently the conversion of α,β-unsaturated cyanohydrins (**1a-c**), obtained by (R)-oxynitrilase catalyzed addition of HCN to α,β-unsaturated aldehydes[3], into both enantiomeric forms of the corresponding 2-hydroxy-3-alkenoic acid esters [(*R*)-**2a-c** and (*S*)-**2a-c**] was described[4] (Scheme 1). The present article relates the use of these products as substrates in asymmetric epoxidation reactions.

Epoxides are among the most versatile intermediates in organic chemistry. They are easily prepared from a variety of starting materials, and can be transformed by a wide range of reagents[5]. Selective oxidation of olefins is the most common and reliable route towards epoxides. The availability of epoxides, especially epoxy alcohols, in enantiopure form, has proven to be of great importance in stereoselective

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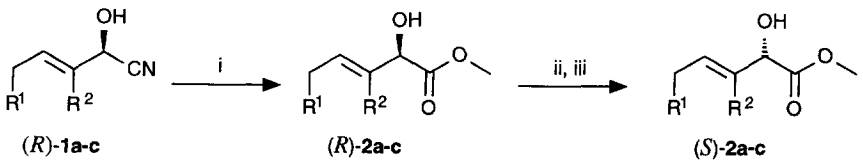


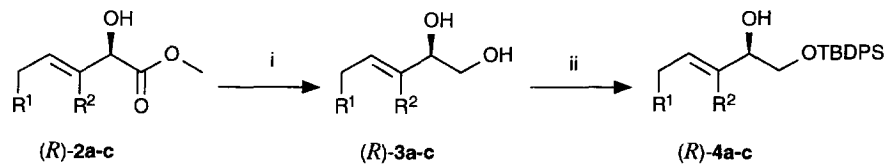
a: $R^1 = R^2 = H$; **b**: $R^1 = H$, $R^2 = Me$; **c**: $R^1,R^2 = -(CH_2)_3-$
i) 1.HCl, MeOH, Et_2O, 2.H_2O ii)Ph_3P, DEAD, AcOH. iii) $MeSO_3H$, MeOH.

Scheme 1: *Synthesis of* (R)*-2 and* (S)*-2.*

organic synthesis. Asymmetric epoxidation of chiral secondary allylic alcohols is generally performed with an organic peracid[6,7] or a peroxide transition metal complex[7,8]. In cases where acyclic allylic alcohols are involved good diastereoselectivities can be achieved when the double bond is *Z*-substituted relative to the chiral centre bearing the alcohol function. With *E*-substituted alkenes lower diastereoselectivities are generally observed[6,7,8]. The Sharpless epoxidation, using enantiomerically pure tartrate esters as a chiral ligand, has found numerous applications in the asymmetric epoxidation of allylic alcohols in non-chiral form, as well as racemic allylic alcohols (e.g. kinetic resolution), and high enantioselectivity has been achieved in many cases[9]. Surprisingly, only few examples have been reported where epoxidation under Sharpless conditions has been applied to enantiomerically pure allylic alcohols[10]. It is to be expected that in such cases both d.e. enhancing (matching) and d.e. decreasing (mismatching) effects, such as known from the kinetic resolution, will be observed with respect to the asymmetric induction obtained in systems with a non-chiral catalyst[9b].

Results and Discussion

Apart from being used as substrates for the epoxidations, the 2-hydroxy-3-enoic acid esters (*R*)-**2a-c** and (*S*)-**2a-c** were also exploited as starting materials for the preparation of two other sets of allylic alcohols, likewise to be used as substrates in asymmetric epoxidations. Esters (*R*)-**2a-c** and (*S*)-**2a-c** were reduced to vicinal diols (*R*)-**3a-c** and (*S*)-**3a-c**. For the (*R*)-enantiomers this is depicted in Scheme 2.

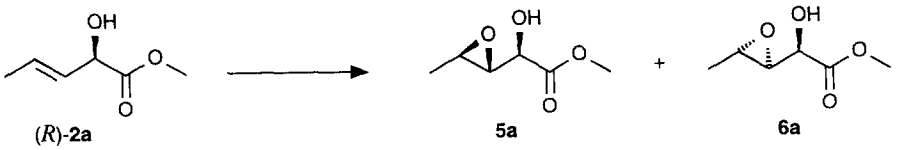


a: $R^1 = R^2 = H$; **b**: $R^1 = H$, $R^2 = Me$; **c**: $R^1,R^2 = -(CH_2)_3-$
i) $LiAlH_4$. ii) TBDPSCl, imidazole.

Scheme 2: *Synthesis and monoprotection of vicinal diols.*

The diols were then selectively mono-protected at the primary hydroxyl group, using 1 equivalent of *tert*-butyldiphenylsilyl chloride (TBDPSCl). The TBDPS-protective group was chosen because of its UV-absorbing properties. This enables determination of the e.e. of mono-protected diols (*R*)-**4a-c** and (*S*)-**4a-c**, and their corresponding epoxides, by chiral HPLC using UV-detection.

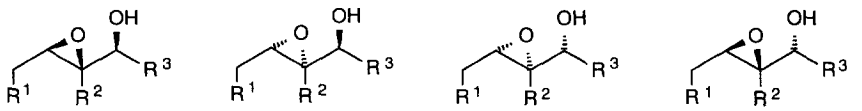
First, the influence of different types of reagents and reaction conditions on the stereoselectivity of the epoxidation was examined with ester (*R*)-**2a**. In order to develop dependable HPLC-analyses it was desired to dispose of both possible stereoisomers of each reaction product. The oxidation experiments were therefore started with the achiral oxidant *m*-chloroperoxybenzoic acid (*m*-CPBA) which was expected to show only modest diastereoselectivity. Epoxidation of (*R*)-**2a** with *m*-CPBA (Scheme 3) afforded two diastereomeric epoxides **5a** and **6a** in a ratio of 2.6 to 1. (Table 1). *A priori* the *threo* isomer **5a** was expected to be the major component[11]. Upon column chromatography diastereomerically pure **5a** was isolated in 47% yield. The fraction containing isomer **6a** still contained some **5a**. The enantiomer of (*R*)-**2a**, compound (*S*)-**2a** with e.e. 97%, was similarly oxidized. *Threo* epoxide **7a** (Scheme 4) was obtained upon *m*-CPBA epoxidation and chromatographic separation of diastereomers in 50% yield.



Scheme 3: m-*CPBA epoxidation of* (R)-*2a.*

In order to verify the correctness of the stereochemical assignments, a pure sample of epoxide **6a** was derivatized into a crystalline compound, suitable for X-ray analysis. This analysis, to be published separately, showed epoxide **6a** to have indeed the *erythro* configuration shown in Scheme 3. This result was extrapolated to all other epoxides by comparing their relative retention times in GC analysis, in accordance with the findings of Mihelich[7a].

When the *m*-CPBA epoxidation conditions were applied to esters **2b** and **2c**, the ratio of the obtained diastereomeric epoxides dropped to almost 1 to 1, presumably due to increased $A_{1,2}$ strain[6b] in **2b** and **2c** compared with **2a**. In these cases the diastereomeric mixtures could not be separated by column chromatography.



a: $R^1 = R^2 = H$; **b**: $R^1 = H$, $R^2 = Me$; **c**: $R^1,R^2 = -(CH_2)_3-$; **5-8**: $R^3 = COOCH_3$; **9-12**: $R^3 = CH_2OTBDPS$

Scheme 4: *Prepared epoxides.*

When the *m*-CPBA epoxidation was performed on the monoprotected vicinal diols (*R*)-**4a-c** and (*S*)-**4a-c**, similar results were obtained, with a slight shift in selectivity in favour of the *erythro* epoxy alcohols. In this case, however, the diastereomeric epoxy alcohols obtained from **4b** and **4c** could be separated by flash chromatography, whereas the isomers obtained from **4a** could not. Nevertheless, this procedure provided the necessary reference materials. The results of the peracid epoxidations are summarized in Table 1.

Table 1: *Results of m-CPBA epoxidations.*

Type of allylic alcohol (e.e.)	ratio of isomeric epoxy alcohols[a]		isolated yields of epoxy alcohols[b]	
	threo	*erythro*	*threo*	*erythro*
(*R*)-**2a** (>99%)	72 (**5a**)	28 (**6a**)	47%	21%
(*R*)-**2b** (>99%)	55 (**5b**)	45 (**6b**)	-	-
(*R*)-**2c** (>99%)	56 (**5c**)	44 (**6c**)	-	-
(*R*)-**4a** (97%)	66 (**9a**)	34 (**10a**)	-	-
(*R*)-**4b** (99%)	41 (**9b**)	59 (**10b**)	37%	54%
(*R*)-**4c** (>99%)	40 (**9c**)	60 (**10c**)	30%	48%

a) Ratio of diastereomers determined by GC. b) Isolated yields of the mixtures obtained from **2b**, **2c**, and **4a** were in the region 70-80%.

For the preparation of the enantiomerically and diastereomerically pure *erythro* epoxy alcohols attention was focused on the Sharpless Asymmetric Epoxidation (SAE), renowned for its *erythro* selectivity in the kinetic resolution of racemic allylic alcohols[9b]. The choice of the tartrate ligand to be used was based on the known stereochemistry of the SAE[9a]. Subjecting (*R*)-**2a** to the Sharpless epoxidation conditions, using (+)-dimethyl tartrate (DMT), provided the desired *erythro* isomer **6a** in 73% isolated yield. (Table 2). GC analysis of the crude product showed the presence of only one diastereomer, indicating complete diastereoselection. Diastereomer **8a**, the enantiomer of **6a**, was similarly obtained upon treatment of (*S*)-**2a** (e.e. 97%) with the Sharpless reagent using (-)-DMT, in 75% yield and with a d.e. of 97%[#].

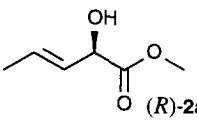
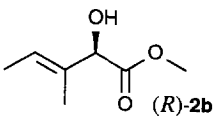
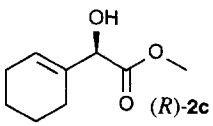
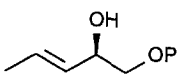
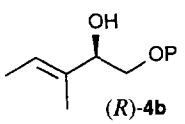
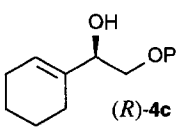
Next, compound (*R*)-**2a** was reacted using (-)-DMT under standard SAE conditions. As expected, epoxidation, using the enantiomeric mismatching tartrate, proceeded much slower (24h versus 4h for the reaction using the matching tartrate) and with low selectivity (60:40 with the *threo* isomer **5a** as the major product). Reaction of (*R*)-**2a** under the same conditions, but in the absence of a tartrate ligand, led to the formation of a 41:59 mixture of diastereomers, with a preference for the *erythro* isomer **6a**.

[#]The 1.5% diastereomeric impurity in **8a** is most likely caused by epoxidation of the enantiomeric impurity present in the starting material (*S*)-**2a** (e.e. 97%) catalyzed by the mismatching tartrate.

Evidently, the high selectivity observed in the epoxidation using the matching tartrate is caused by the asymmetric catalytic species.

Following these results, the other substrates were subjected to the conditions of the Sharpless asymmetric epoxidation, as well as to the procedure without tartrate. The results obtained with the (*R*)-enantiomers are presented in Table 2.

Table 2: *Results of the Sharpless asymmetric epoxidation of compounds* (R)-***2a-c*** *and* (R)- ***4a-c***.

Substrate[a]	Tartrate used in epoxidation[b]			Isolated epoxides[d]		
	(+)-DMT	(-)-DMT	none	d.e. (%)	e.e. (%)	yield
	T/E[c]	*T/E*[c]	*T/E*[c]			
 (*R*)-**2a**	> 1:99	60:40	41:59	> 99	> 99	73% **6a**
 (*R*)-**2b**	1:99	28:72	21:79	98	> 99	86% **6b**
 (*R*)-**2c**	62:38	7:93	7:93	89	> 99	73% **6c**
 (*R*)-**4a**	3:97	-	42:58	93	> 99	82% **10a**
 (*R*)-**4b**	> 1:99	-	21:79	> 99	99	81% **10b**
 (*R*)-**4c**	> 1:99	> 1:99	> 1:99	> 99	> 99	82% **10c**

a) E.e. of (*R*)-**2a-c** and (*R*)-**4c** > 99%, (*R*)-**4a** 97%, and (*R*)-**4b** 99%. b) Reagents: $Ti(OPr)_4$/TBHP. c) *Threo/Erythro* ratios determined by GC analysis. d) *Erythro* epoxides, prepared via the optimum procedure for each individual compound.

Apparently, the acyclic substrates **2a-b** and **4a-b** can be converted into the *erythro* epoxy alcohols with excellent stereoselectivity by the Sharpless asymmetric epoxidation procedure, using the proper tartrate. For the more sterically demanding cyclic compounds **2c** and **4c** however, the situation is radically different and high (**2c**) or even complete (**4c**) *erythro* selectivity is obtained by direct asymmetric induction, i.e. Sharpless epoxidation in the **absence** of added chiral ligand. For compound **2c** the SAE procedure using (+)-DMT gave an inversed selectivity in favour of the *threo* isomer. Initially interpretation of these results was troubled by the high *erythro* selectivity observed in the presence of the supposedly mismatching tartrate. Identification of the absolute configuration of the obtained *erythro* epoxy alcohol **6c** by X-ray analysis of its 4-nitrobenzoate however made it clear that the assigned configurations were correct. It therefore appears that the observed high selectivities for the catalyst complex in the presence of the mismatching (-)-DMT are in fact caused by a catalytic species in which the tartrate ester plays no significant role. Support for this statement is found in the equally high selectivities observed in the epoxidation reactions without tartrate.

In order to check whether these same epoxides could be produced by kinetic resolution of the 2-hydroxy-3-alkenoic esters, some kinetic resolution experiments on racemic methyl (*E*)-2-hydroxy-3-pentenoate using (+)-dimethyl tartrate and (+)-diisopropyl tartrate were performed. Kinetic resolution using (+)-DMT gave at a conversion of 50% a 28:72 ratio of diastereomers and left unreacted hydroxy ester with an e.e. of 29%. These results indicate a relatively small rate difference in the epoxidation of the enantiomers of methyl (*E*)-2-hydroxy-3-pentenoate under these conditions. Kinetic resolution with (+)-DIPT[9] was more successful as it produced a 6:94 ratio of diastereomers and left unreacted hydroxy ester with an e.e. of 77%.

It is of interest to note that in this case an allylic alcohol, which is apparently not a good substrate in kinetic resolution experiments, shows very high stereoselection when used in enantiomerically pure form. As expected, the results obtained in the metal-catalyzed peroxide oxidations of the enantiomeric series (*S*)-**2a-c** and (*S*)-**4a-c** were virtually identical to those observed in the corresponding (*R*)-series. The small differences noticed (see experimental part) were obviously caused by the slightly lower e.e. values of the starting materials.

Conclusion

It can be stated that achiral peracid oxidation of two series of chiral allylic alcohols proceeded with modest selectivity towards formation of the *threo* isomer. In several, but not in all, cases the pure *threo* compounds could be isolated by column chromatography.

Titanium catalyzed peroxide oxidation in the presence of the matching chiral tartrate proceeded with high or even complete *erythro* selectivity in all cases. In the case of the more encumbered cyclohexenyl compounds, **2c** and **4c**, addition of tartrate was not needed, as equal or higher selectivities were observed in the absence of chiral ligand. All *erythro* isomers were isolated in nearly enantiomerically and diastereomerically pure form.

Experimental

Enantiomeric purities were determined by HPLC using a *Chiralcel OD* column. As eluents mixtures of hexane (H) and *iso*-propanol (I), which are specified in each case, were applied. Diastereomeric purity of epoxides was determined by GC using a *Chrompack CP-SIL-19 CB* column (25 m x 0.22 mm, carrier

gas N_2). Temperatures are specified for each compound. Optical rotations were measured using a *Propol* automatic polarimeter. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a *JEOL FX-200* instrument. Samples were measured in $CDCl_3$, with Me_4Si as an internal standard for ^{1}H-NMR, and $CDCl_3$ as an internal standard for ^{13}C-NMR; δ in ppm, J in Hz.

The preparation of cyanohydrins **1a-c** and 2-hydroxy-3-enoic acid esters **2a-c** has been reported recently[4]. E.e.'s: (*R*)-**2a** >99%, (*R*)-**2b** >99%, (*R*)-**2c** >99%, (*S*)-**2a** 97%, (*S*)-**2b** 97%, (*S*)-**2c** 98%.

Lithium aluminum hydride reduction:

To a suspension of $LiAlH_4$ (3.8 g, 100 mmol) in dry THF (100 ml) was added dropwise a soln. of hydroxy ester **2** (100 mmol) in THF (50 ml) over a 30 min period, after which the mixture was refluxed for 1 h. The mixture was cooled in an ice-bath and H_2O (3.8 ml) in THF (27 ml), 15% aq. NaOH soln. (3.8 ml), and H_2O (11.4 ml) were sequentially added. The mixture was stirred until a fine white precipitate was formed, which was filtered off and washed with THF. The organic solvent was dried and evaporated.

(-)-(2*R*,3*E*)-3-Penten-1,2-diol ((*R*)-**3a**) was prepared from (*R*)-**2a** (13 g, 100 mmol): 8.7 g (85%) of (*R*)-**3a** as a colourless oil. B.p. 52 °C, 0.22 mm Hg. $[\alpha]_D^{20}$ = -23.4 (c = 1, $CHCl_3$). ^{1}H-NMR: 1.73 (d, 3 H-C(5)), 2.12 (br., 2 OH), 3.49 (dd, ABX, J_{ab} = 11.3, J_{ax} = 7.2, 1 H-C(1)), 3.64 (dd, ABX, J_{ab} = 11.3, J_{bx} = 3.6, 1 H-C(1)), 4.19 (m, H-C(2)), 5.48 (m, H-C(3)), 5.80 (m, H-C(4)). ^{13}C-NMR: 17.6 (C(5)), 66.1 (C(1)), 72.8 (C(2)), 128.0, 129.5.

(-)-(2*R*,3*E*)-3-Methyl-3-penten-1,2-diol ((*R*)-**3b**) was prepared from (*R*)-**2b** (2.6 g, 20 mmol): 2.3 g (99%) of (*R*)-**3b** as a colourless oil. $[\alpha]_D^{20}$ = -22.0 (c = 1, $CHCl_3$). ^{1}H-NMR: 1.62 (s, 3-Me), 1.65 (d, 3 H-C(5)), 2.64 (br., 2 OH), 3.52 (dd, ABC, J_{ab} = 11.3, J_{ac} = 7.7, 1 H-C(1)), 3.62 (dd, ABC, J_{ab} = 11.3, J_{bc} = 4.1, 1 H-C(1)), 4.13 (m, H-C(2)), 5.57 (q, H-C(4)). ^{13}C-NMR: 12.1 (3-Me), 12.8 (C(5)), 65.3 (C(1)), 77.2 (C(2)), 121.0 (C(4)), 134.4 (C(3)).

(-)-(2*R*)-1-(Cyclohex-1-enyl)-ethan-1,2-diol ((*R*)-**3c**) was prepared from (*R*)-**2c** (3.4 g, 20 mmol): 2.7 g (96%) of (*R*)-**3c** as a white solid. M.p. 69 °C. $[\alpha]_D^{20}$ = -27.0 (c = 1, $CHCl_3$). ^{1}H-NMR: 1.60 (m, 4 H), 2.03 (m, 4 H), 2.40 (br., 2 OH), 3.54 (dd, ABC, J_{ab} = 11.3, J_{ac} = 7.7, 1 H-C(2)), 3.64 (dd, ABC, J_{ab} = 11.3, J_{bc} = 3.6, 1 H-C(2)), 4.07 (m, H-C(1)), 5.76 (br., H-C(2')). ^{13}C-NMR: 22.3, 22.4, 24.7, 24.8, 65.4 (C(2)), 76.1 (C(1)), 123.3 (C(2')), 136.5 (C(1')).

(+)-(2*S*,3*E*)-3-Penten-1,2-diol ((*S*)-**3a**) was prepared from (*S*)-**2a** (1.7 g, 13 mmol): 1 g (78%) of (*S*)-**3a** as a colourless oil. $[\alpha]_D^{20}$ = +15.9 (c = 1, $CHCl_3$). Anal. data: in agreement with those for (*R*)-**3a**.

(+)-(2S,3E)-3-Methyl-3-penten-1,2-diol ((*S*)-**3b**) was prepared from (*S*)-**2b** (1.9 g, 13 mmol): 1.4 g (94%) of (*S*)-**3b** as a colourless oil. $[\alpha]_D^{20}$ = +21.6 (c = 0.8, $CHCl_3$). Anal. data: in agreement with those for (*R*)-**3b**.

(+)-(2*S*)-1-(Cyclohex-1-enyl)-ethan-1,2-diol ((*S*)-**3c**) was prepared from (*S*)-**2c** (0.5 g, 3 mmol): 0.4 g (92%) of (*S*)-**3c** as a white solid. $[\alpha]_D^{20}$ = +28.0 (c = 0.4, $CHCl_3$). Anal. data: in agreement with those for (*R*)-**3c**.

Mono-protection of diols; general procedure:

To a soln. of imidazole (4.76 g, 70 mmol) in DMF (200 ml) at 0 °C was added *tert*-butyldiphenylsilyl chloride (TBDPSCl) (11.0 g, 40 mmol) and the mixture was allowed to react for 10

min after which diol **3** (40 mmol) was added. The mixture was stirred for 18 h at r.t., poured out in H_2O (300 ml), and extracted with Et_2O (3 x 100 ml). The combined organic layers were washed with brine (2 x 50 ml), dried ($MgSO_4$) and the solvent evaporated. The crude product was chromatographed (silica gel, EtOAc/light petroleum 1:19).

(-)-(2*R*,3*E*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3-penten-2-ol ((*R*)-**4a**) was prepared from (*R*)-**3a** (4.1 g, 40 mmol): 10.9 g (80%) of (*R*)-**4a** as a colourless oil. $[\alpha]_D^{20}$ = -8.1 (c = 1, $CHCl_3$); e.e. 97% (HPLC eluent H:I = 97:3, 0.5 ml/min, 254 nm). ^{1}H-NMR: 1.07 (s, Me_3C), 1.67 (d, 3 H-C(5)), 2.65 (br., OH), 3.51 (dd, ABC, J_{ab} = 10.3, J_{ac} = 7.7, 1 H-C(1)), 3.65 (dd, ABC, J_{ab} = 10.3, J_{bc} = 3.6, 1 H-C(1)), 4.20 (br., H-C(2)), 5.38 (m, H-C(3)), 5.73 (m, H-C(4)), 7.34-7.41 (m, 6 H-arom), 7.64-7.69 (m, 4 H-arom). ^{13}C-NMR: 17.7 (C(5)), 19.3 (Me_3C), 26.7 (Me_3C), 67.9 (C(1)), 72.7 (C(2)), 127.6, 128.3 (C(3)), 129.5 (C(4)), 129.7, 133.1 (C_{ipso}), 135.4.

(-)-(2*R*,3*E*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3-methyl-3-penten-2-ol ((*R*)-**4b**) was prepared from (*R*)-**3b** (2.3 g, 20 mmol): 5.7 g (81%) of (*R*)-**4b** as a colourless oil. $[\alpha]_D^{20}$ = -6.2 (c = 1, $CHCl_3$); e.e. 99% (HPLC H:I = 99:1, 0.5 ml/min, 254 nm). ^{1}H-NMR: 1.07 (s, Me_3C), 1.51 (s, 3-Me), 1.57 (d, 3 H-C(5)), 2.67 (d, OH), 3.58 (dd, ABC, J_{ab} = 10.3, J_{ac} = 7.7, 1 H-C(1)), 3.67 (dd, ABC, J_{ab} = 10.3, J_{bc} = 4.1, 1 H-C(1)), 4.12 (m, H-C(2)), 5.52 (m, H-C(4)), 7.34-7.46 (m, 6 H-arom), 7.64-7.69 (m, 4 H-arom). ^{13}C-NMR: 12.0 (3-Me), 12.9 (C(5)), 19.2 (Me_3C), 26.8 (Me_3C). 66.8 (C(1)), 76.9 (C(2)), 121.5 (C(4)), 127.7, 129.7, 133.5 (C(3)), 134.0 (C_{ipso}), 135.5.

(-)-(2*R*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-1-(cyclohex-1-enyl)-ethan-2-ol ((*R*)-**4c**) was prepared from (*R*)-**3c** (0.75 g, 5.2 mmol): 1.63 g (83%) of (*R*)-**4c**. Colourless oil. $[\alpha]_D^{20}$ = -3.1 (c = 1, $CHCl_3$); e.e. 99% (HPLC eluent H:I = 99:1, 1 ml/min, 254 nm). ^{1}H-NMR: 1.07 (s, Me_3C), 1.54 (m, 4 H), 1.99 (m, 4 H), 2.69 (br., OH), 3.59 (dd, ABC, J_{ab} = 9.8, J_{ac} = 7.7, 1 H-C(2)), 3.69 (dd, ABC, J_{ab} = 9.8, J_{bc} = 4.1, 1 H-C(2)), 4.08 (br., H-C(1)), 5.70 (br., H-C(2')), 7.39 (m, 6 H-arom), 7.67 (m, 4 H-arom). ^{13}C-NMR: 19.2 (Me_3C), 22.4, 22.5, 24.6, 24.8, 26.8 (Me_3C), 66.9 (C(2)), 75.8 (C(1)), 123.8 (C(2')), 127.7, 129.7, 133.2 (C_{ipso}), 135.5, 136.1 (C(1')).

(+)-(2*S*,3*E*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3-penten-2-ol ((*S*)-**4a**) was prepared from (*S*)-**3a** (1,0 g, 10 mmol): 2.1 g (62%) of (*S*)-**4a** as a colourless oil. $[\alpha]_D^{20}$ = +6.6 (c = 1, $CHCl_3$); e.e. 89% (HPLC, eluent H:I = 97:3, 0.5 ml/min, 254 nm). Anal. data: in agreement with those for (*R*)-**4a**.

(+)-(2S,3E)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3-methyl-3-penten-2-ol ((*S*)-**4b**) was prepared from (*S*)-**3b** (1.3 g, 11 mmol): 3.2 g (81%) of (*S*)-**4b** as a colourless oil. $[\alpha]_D^{20}$ = +5.9 (c = 1, $CHCl_3$); e.e. 98% (HPLC, eluent H:I = 99:1, 0.5 ml/min, 254 nm). Anal. data: in agreement with those for (*R*)-**4b**.

(+)-(2*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-1-(cyclohex-1-enyl)-ethan-2-ol ((*S*)-**4c**) was prepared from (*S*)-**3c** (0.37 g, 2.6 mmol): 0.67 g (69%) of (*S*)-**4c** as a colourless oil. $[\alpha]_D^{20}$ = +2.8 (c = 0.6, $CHCl_3$); e.e. 98% (HPLC, eluent H:I = 99:1, 1 ml/min, 254 nm). Anal. data: in agreement with those for (*R*)-**4c**.

General epoxidation procedures:

***m*-CPBA Epoxidation:** Technical grade *m*-CPBA, (3.6 g, ca. 16 mmol) was dissolved in CH_2Cl_2 (40 ml) and added dropwise to a soln. of the allylic alcohol (10 mmol) in CH_2Cl_2 (40 ml). The reaction was monitored TLC. After completion the reaction mixture was washed subsequently with saturated $NaHCO_3$ (20 ml), and brine (10 ml). After drying (Na_2SO_4) and evaporation of the solvent the crude mixture of diastereomers was obtained as a pale yellow oil. The diastereomers mixtures **5a/6a**, **7a/8a**, **9b/10b**,

9c/10c, **11b/12b**, and **11c/12c** were separated by chromatography (silica gel, EtOAc/light petroleum 1:4 for **5a/6a** and **7a/8a**, and 1:19 for all other compounds).

Catalytic Sharpless Asymmetric Epoxidation: In dichloromethane (50 ml) (distilled from CaH_2 and stored on molsieves 4Å) dimethyl tartrate (DMT) (0.18 g, 1 mmol) was dissolved in the presence of a small amount of activated molsieves (4Å). At -10 °C titanium tetraisopropoxide (0.15 ml, 0.5 mmol) was added. After 45 min the allylic alcohol (5 mmol) and 3M *t*-butylhydroperoxide solution (4 ml) were added. The reaction was allowed to warm to r.t., and was monitored by TLC. After completion a 5% (w/v) tartaric acid solution (10 ml) was added. After stirring for one hour the layers were separated, the organic layer was dried (Na_2SO_4), and the solvent evaporated. The crude product was chromatographed (silica gel, EtOAc/light petroleum 1:3 for **6** and **8**, 1:9 for **10** and **12**).

Titanium Catalyzed Epoxidation: In dichloromethane (50 ml) (distilled from CaH_2 and stored on molsieves 4Å) the allylic alcohol (5 mmol) was dissolved in the presence of a small amount of activated molsieves (4Å). At -10 °C titanium tetraisopropoxide (0.15 ml, 0.5 mmol) was added. After 30 min 3M *t*-butylhydroperoxide solution (4 ml) was added. The reaction was allowed to warm to r.t., and was monitored by TLC. After completion a 5% (w/v) tartaric acid solution (10 ml) was added. After stirring for one hour the layers were separated, the organic layer was dried (Na_2SO_4), and the solvent evaporated. The crude product was chromatographed (silica gel, EtOAc/light petroleum 1:3 for **6c** and **8c**, 1:9 for **10c** and **12c**).

Methyl (+)-(2*R*,3*S*,4*R*)-2-hydroxy-3,4-oxapentanoate (**5a**), (*threo* isomer) was prepared from (*R*)-**2a** by the *m*-CPBA procedure (*vide supra*): 0.69 g (47%) of **5a** as a colourless oil. $[\alpha]_D^{20}$ = +23.9 (c = 1, $CHCl_3$); e.e. 99% (HPLC eluent H:I = 97:3, 1 ml/min, 220 nm), d.e. 99% (GC, 100 °C). ^{1}H NMR: 1.35 (d, J = 5.4, 3 H-C(5)); 2.90 (br., OH); 3.06 ('dd', $J_1 = J_2$ = 2.5, H-C(3)); 3.21 (dq, J_1 = 5.4, J_2 = 2.5, H-C(4)); 3.85 (s, MeO); 4.33 (d, J = 2.5, H-C(2)). ^{13}C NMR: 16.1 (C(5)); 50.9 (C(4)); 51.9 (MeO); 58.9 (C(3)); 68.7 (C(2)); 171.8 (C=O). The second fraction (0.31 g, 21%) was a mixture of *threo/erythro* isomers in a ratio of 15/85 (NMR).

Methyl (-)-(2*R*,3*R*,4*S*)-2-hydroxy-3,4-oxapentanoate (**6a**), (*erythro* isomer) was prepared from (*R*)-**2a** by the Sharpless procedure (*vide supra*) using (+)-DMT: 0.53 g (73%) of **6a** as a colourless oil. $[\alpha]_D^{20}$ = -45.5 (c = 1, $CHCl_3$); e.e. > 99% (HPLC eluent H:I = 97:3, 1 ml/min, 220 nm), d.e. >99% (GC, 100 °C). ^{1}H NMR: 1.34 (d, J = 5.1, 3 H-C(5)); 2.78 (d, J = 4.1, OH); 2.98 (dd, J_1 = 4.1, J_2 = 2.1, H-C(3)); 3.13 (dq, J_1 = 5.1, J_2 = 2.1, H-C(4)); 3.86 (s, MeO); 4.27 ('dd', $J_1 = J_2$ = 4.1, H-C(2)). ^{13}C NMR: 15.9 (C(5)); 50.7 (C(4)); 51.5 (MeO); 58.0 (C(3)); 68.8 (C(2)); 171.3 (C=O).

Methyl (-)-(2*R*,3*R*,4*S*)-2-hydroxy-3-methyl-3,4-oxapentanoate (**6b**), (*erythro* isomer) was prepared from (*R*)-**2b** by the Sharpless procedure (*vide supra*) using (+)-DMT: 0.68 g (86%) of **6b** as a colourless oil. $[\alpha]_D^{20}$ = -82.4 (c = 1, $CHCl_3$); e.e. > 99% (HPLC eluent H:I = 95:5, 0.5 ml/min, 220 nm), d.e. ≥ 98% (GC, 130 °C). ^{1}H-NMR: 1.29 (s, 3-Me), 1.33, (d, 3 H-C(5)), 3.04 (d, OH), 3.11 (q, H-C(4)), 3.86 (s, MeO), 3.89 (d, H-C(2)). ^{13}C-NMR: 12.1 (3-Me), 13.0(C(5)), 51.9 (MeO), 56.4 (C(4)), 59.8 (C(3)), 74.5 (C(2)), 172.1 (C=O).

Methyl (-)-(2*R*,1'*R*,2'*S*)-2-(cyclohexan-1,2-oxide)-2-hydroxyacetate (**6c**), (*erythro* isomer) was prepared from (*R*)-**2c** by the titanium procedure (*vide supra*): 0.68 g (73%) of **6c** as a colourless oil. $[\alpha]_D^{20}$ = -70.6

(c = 1, $CHCl_3$); e.e. > 99% (HPLC eluent H:I = 95:5, 1 ml/min, 220 nm), d.e. 89% (GC, 150 °C). ^{1}H-NMR: 1.22-2.06 (m, 8 H), 3.02 (d, OH), 3.21 (d, H-C(2)), 3.85 (s, MeO), 3.88 (t, H-C(2')). ^{13}C-NMR: 18.7, 19.7, 23.3, 24.1, 52.4 (MeO), 56.6 (C(2')), 59.3 (C(1')), 74.2 (C(2)), 172.4 (C=O).

Methyl (-)-(2*S*,3*R*,4*S*)-2-hydroxy-3,4-oxapentanoate (7a), (*threo* isomer) was prepared from (*S*)-**2a** by the *m*-CPBA procedure (*vide supra*): 0.73 g (50%) of **7a** as a colourless oil. $[\alpha]_D^{20}$ = -24.2 (c = 1, $CHCl_3$); e.e. 96% (HPLC eluent H:I = 97:3, 1 ml/min, 220 nm), d.e. 97% (GC, 100 °C). Anal. data: in agreement with those for **5a**.

Methyl (+)-(2*S*,3*S*,4*R*)-2-hydroxy-3,4-oxapentanoate (8a), (*erythro* isomer) was prepared from (*S*)-**2a** by the Sharpless procedure (*vide supra*) using (-)-DMT: 0.55 g (75%) of **8a** as a colourless oil. $[\alpha]_D^{20}$ = +42.1 (c = 1, $CHCl_3$); e.e. 96% (HPLC eluent H:I = 97:3, 1 ml/min, 220 nm), d.e. 97% (GC, 100 °C). Anal. data: in agreement with those for **6a**.

Methyl (+)-(2*S*,3*S*,4*R*)-2-hydroxy-3-methyl-3,4-oxapentanoate (8b), (*erythro* isomer) was prepared from (*S*)-**2b** by the Sharpless procedure (*vide supra*) using (-)-DMT: 0.68 g (86%) of **8b** as a colourless oil. $[\alpha]_D^{20}$ = +82.4 (c = 1, $CHCl_3$); e.e. > 99% (HPLC eluent H:I = 95:5, 0.5 ml/min, 220 nm), d.e. ≥ 96% (GC, 130 °C). Anal. data: in agreement with those for **6b**.

Methyl (+)-(2*S*,1'*S*,2'*R*)-2-(cyclohexan-1,2-oxide)-2-hydroxyacetate (8c), (*erythro* isomer) was prepared from (*S*)-**2a** by the titanium procedure (*vide supra*): 0.73 g (77%) of **8c** as a colourless oil. $[\alpha]_D^{20}$ = +69.5 (c = 1, $CHCl_3$); e.e. > 98% (HPLC eluent H:I = 95:5, 1 ml/min, 220 nm), d.e. 90% (GC, 150 °C). Anal. data: in agreement with those for **6c**.

(+)-(2*R*,3*S*,4*R*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3-methyl-3,4-oxapentan-2-ol (9b) was prepared from (*R*)-**4b** (0.70 g, 2 mmol) by the *m*-CPBA procedure (*vide supra*): 0.27 g (37%) as a colourless oil. $[\alpha]_D^{20}$ = +5.0 (c = 1, $CHCl_3$); e.e. 99% (HPLC eluent H:I = 99:1, 0.5 ml/min, 254 nm), d.e. 99% (GC, 220 °C). ^{1}H-NMR: 1.06 (s, Me_3C); 1.22 (s, 3-Me); 1.27 (d, *J* = 5.6, 3 H-C(5)); 2.60 (d, *J* = 4.1, OH); 3.02 (q, *J* = 5.6, H-C(4)); 3.46 (dd, *J* = 4.1, *J* = 5.7, H-C(2)); 3.72 (d, *J* = 5.7, 2 H-C(1)); 7.41 (m, 6 H-arom); 7.66 (m, 4 H-arom). ^{13}C-NMR: 11.5 (3-Me); 13.3 (C(5)); 19.0 (Me_3C); 26.7 (Me_3C); 56.8 (C(4)); 61.7 (C(3)); 64.5 (C(1)); 76.2 (C(2)); 127.6 (C-arom); 129.7 (C-arom); 132.9 (C_{ipso}); 135.4 (C-arom). The second fraction (0.40 g, 54%) contained the other isomer (**10b**, e.e. 99%, d.e. 99%).

(+)-(2*R*,1'*S*,2'*R*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-2-(cyclohexan-1,2-oxide)-ethan-2-ol (9c) was prepared from (*R*)-**4c** (0.50 g, 1.3 mmol) by the *m*-CPBA procedure (*vide supra*): 0.15 g (30%) as a colourless oil. $[\alpha]_D^{20}$ = +5.9 (c = 1.6, $CHCl_3$); e.e. 99%, d.e. 99% (HPLC eluent H:I = 99:1, 0.5 ml/min, 254 nm). ^{1}H-NMR: 1.06 (Me_3C); 1.12-54 (m, 4 H); 1.64-2.06 (m, 4 H); 3.19 (d, *J* = 2.8, H-C(2')); 3.57 (t, *J* = 5.6, H-C(2)); 3.75 (m, 2 H-C(1)); 7.42 (m, 6 H-arom) 7.66 (m, 4 H-arom). ^{13}C-NMR: 19.1 (Me_3C); 19.4; 19.7; 23.4; 24.2; 26.7 (Me_3C); 56.2 (C(2')); 61.0 (C(1')); 64.4 C(1)); 75.2 (C(2)); 127.6 (C-arom); 129.7 (C-arom); 133.0 (C_{ipso}); 135.4 (C-arom). The second fraction (0.22 g, 48%) contained the other isomer (**10c**, e.e. 99%, d.e. 99%).

(-)-(2*R*,3*R*,4*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3,4-oxapentan-2-ol (10a) was prepared from (*R*)-**4a** by the Sharpless procedure (*vide supra*) using (+)-DMT, and EtOAc/light petroleum 1:9 as eluent for chromatography: 1.5 g (82%) of **10a** as a colourless oil. $[\alpha]_D^{20}$ = -4.3 (c = 1, $CHCl_3$); e.e. > 99% (HPLC eluent H:I = 95:5, 1 ml/min, 254 nm), d.e. 93% (GC, 220 °C). ^{1}H-NMR: 1.07 (s, Me_3C), 1.33 (d, 3 H-C(5)), 2.38 (d, OH), 2.80 (dd, J_1 = 2.6, J_2 = 5.1, H-C(3)), 3.05 (dq, J_1 = 2.1, J_2 = 5.1, H-C(4)), 3.66 (m, H-C(2)), 3.79 (d, *J* = 4.6, 2 H-C(1)), 7.41 (m, 6 H-arom), 7.66 (m, 4 H-arom). ^{13}C-NMR: 17.1 (C(5)), 19.1 (Me_3C), 26.7 (Me_3C), 51.9 (C(4)), 59.2 (C(3)), 65.2 (C(1)), 70.4 (C(2)), 127.6, 129.7, 132.8 (C_{ipso}),

135.3

(-)-(2*R*,3*R*,4*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3-methyl-3,4-oxapentan-2-ol (10b) was prepared from (*R*)-**4b** by the Sharpless procedure (*vide supra*) using (+)-DMT, and EtOAc/light petroleum 1:9 as eluent for chromatography: 1.5 g (81%) of **10b** as a colourless oil. $[\alpha]_D^{20}$ = -2.1 (c = 1, $CHCl_3$); e.e. 99% (HPLC eluent H:I = 99:1, 0.5 ml/min, 254 nm), d.e. > 99% (GC, 220 °C). ^{1}H-NMR: 1.06 (s, Me_3C); 1.25 (s, 3-Me); 1.30 (d, *J* = 5.1, 3 H-C(5)); 2.47 (d, *J* = 2.1, OH); 3.18 (q, *J* = 5.1, H-C(4)); 3.67 (m, H-C(2)); 3.75 (m, 2 H-C(1)); 7.42 (m, 6 H-arom); 7.67 (m, 4 H-arom). ^{13}C-NMR: 13.4 (3-Me); 14.0 (C(5)); 19.1 (Me_3C); 26.7 (Me_3C); 55.7 (C(4)); 60.7 (C(3)); 64.6 (C(1)); 73.8 (C(2)); 127.6 (C-arom); 129.7 (C-arom); 133.0 (C_{ipso}); 135.4 (C-arom).

(-)-(2*R*,1'*R*,2'*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-2-(cyclohexan-1,2-oxide)-ethan-2-ol (10c) was prepared on a 2 mmol scale from (*R*)-**4c** by the titanium procedure (*vide supra*): 0.65 g (82%) of **10c** as a colourless oil. $[\alpha]_D^{20}$ = -6.0 (c = 1, $CHCl_3$); e.e. 99%, d.e. > 99% (HPLC eluent H:I = 99:1, 0.5 ml/min, 254 nm). ^{1}H-NMR: 1.07 (s, Me_3C); 1.26-1.50 (m, 4 H); 1.64-2.04 (m, 4 H); 2.55 (d, *J* = 2.1, OH); 3.24 (m, H-C(2')); 3.61 (dt, J_1 = 2.1, J_2 = 4.6, H-C(2)); 3.78 (d, *J* = 4.6, 2 H-C(1)); 7.41 (m, 6 H-arom); 7.68 (4 H-arom). ^{13}C-NMR: 19.1 (Me_3C); 19.5; 20.0; 24.3; 24.8; 26.7 (Me_3C); 56.2 (C(2')); 60.1 (C(1')); 64.7 (C(1)); 73.2 (C(2)); 127.6 (C-arom); 129.6 (C-arom); 133.0 (C_{ipso}); 135.5 (C-arom).

(-)-(2*S*,3*R*,4*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3-methyl-3,4-oxapentan-2-ol (11b) was prepared from (*S*)-**4b** (0.71 g, 2 mmol) by the *m*-CPBA procedure (*vide supra*): 0.24 g (33%) as a colourless oil. $[\alpha]_D^{20}$ = -3.7 (c = 1, $CHCl_3$); e.e. 97% (HPLC eluent H:I = 99:1, 0.5 ml/min, 254 nm), d.e. 99% (GC, 220 °C). Anal. data: in agreement with those for **9b**. The second fraction (0.32 g, 44%) contained the other isomer (**12b**).

(-)-(2*S*,1'*R*,2'*S*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-2-(cyclohexan-1,2-oxide)-ethan-2-ol (11c) was prepared from (*S*)-**4c** (1.2 g, 3.1 mmol) by the *m*-CPBA procedure (*vide supra*): 0.31 g (25%) as a colourless oil. $[\alpha]_D^{20}$ = -5.8 (c = 1, $CHCl_3$); e.e. 97%, d.e. 95% (HPLC eluent H:I = 99:1, 0.5 ml/min, 254 nm). Anal. data: in agreement with those for **9c**.

(+)-(2*S*,3*S*,4*R*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3,4-oxapentan-2-ol (12a) was prepared from (*S*)-**4a** by the Sharpless procedure (*vide supra*) using (-)-DMT, and EtOAc/light petroleum 1:9 as eluent for chromatography: 1.46 g (82%) of **12a** as a colourless oil. $[\alpha]_D^{20}$ = +4.1 (c = 1, $CHCl_3$); e.e. 93% (HPLC eluent H:I = 95:5, 1 ml/min, 254 nm), d.e. 90% (GC, 220°C). Anal. data: in agreement with **10a**.

(+)-(2*S*,3*S*,4*R*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-3-methyl-3,4-oxapentan-2-ol (12b) was prepared from (*S*)-**4b** (1.76 g, 5 mmol) by the Sharpless procedure (*vide supra*) using (-)-DMT, and EtOAc/light petroleum 1:9 as eluent for chromatography: 1.42 g (78%) of **12b** as a colourless oil. $[\alpha]_D^{20}$ = +2.8 (c = 1, $CHCl_3$); e.e. 98% (HPLC eluent H:I = 99:1, 0.5 ml/min, 254 nm), d.e. 99% (GC, 220 °C). Anal. data: in agreement with those for **10b**.

(+)-(2*S*,1'*S*,2'*R*)-1-[(*tert*-Butyldiphenylsilyl)oxy]-2-(cyclohexan-1,2-oxide)-ethan-2-ol (12c) was prepared on a 2 mmol scale from (*S*)-**4c** by the titanium procedure (*vide supra*): 0.65 g (82%) of **12c** as a colourless oil. $[\alpha]_D^{20}$ = +5.9 (c = 1, $CHCl_3$); e.e. 98%, d.e. 99% (HPLC eluent H:I = 99:1, 0.5 ml/min, 254 nm).

References and Notes

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11. Peracid epoxidations of allylic alcohols are expected to show a preference for the formation of the *threo* epoxides, see refs. 6 and 8.

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