

# Regioselective Ene Reaction in the Photooxygenation of Symmetrically Tetrasubstituted Ethenes and the Ti(IV)-Catalyzed Epoxy-Hydroxylation of Their Allylic Hydroperoxides

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Received May 20, 1988

The photooxygenation of the 1,4-disubstituted 2,3-dimethyl-2-butenes 1–4 [1,4-dichloro, -dibromo, -dimethoxy, and -bis(trimethylsilyl)], respectively afforded the corresponding allylic hydroperoxides 1a–4a via regioselective ene reaction exclusively of the methyl hydrogens. The dichloro derivative 1 gave on photooxygenation in the presence of titanium tetraisopropoxide the desired epoxy alcohol 1b in fair yield (42%), along with the allylic alcohol 1c. The epoxy-hydroxylation of the dibromo derivative 2 turned out to be problematic. Photooxygenation in the presence of Ti(OiPr)<sub>4</sub> ("one-pot" procedure) led to a complex product mixture, from which the allylic alcohol 2c, the dioxolane 2d, and the rearranged epoxy alcohol 2b were isolated. The structure of the latter was rigorously confirmed by an X-ray analysis. Separate treatment of the allylic hydroperoxide 2a with Ti(OiPr)<sub>4</sub> gave a similar complex product mixture.

## Regioselective Ene-Reaktion bei der Photooxygenierung von symmetrisch tetrasubstituierten Ethenen und die Ti(IV)-katalysierte Epoxyhydroxylierung ihrer Allylhydroperoxide

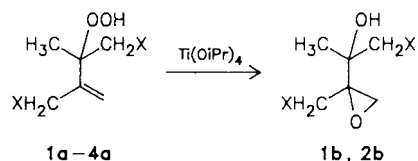
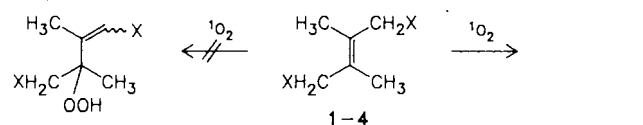
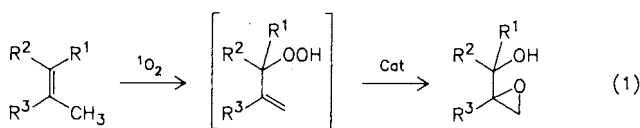
Die Photooxygenierung von 1,4-Dichlor-, 1,4-Dibrom-, 1,4-Dimethoxy- und 1,4-Bis(trimethylsilyl)-2,3-dimethyl-2-buten (1–4) ergab durch ausschließlich über die Methylwasserstoffe verlaufende Ene-Reaktion die Allylhydroperoxide 1a–4a. Das Dichlorderivat 1 lieferte bei der Photooxygenierung in Gegenwart von Titan-tetraisopropylat neben dem Allylalkohol 1c den erwarteten Epoxyalkohol 1b mit mäßiger Ausbeute (42%). Die Epoxyhydroxylierung des Dibromderivats 2 erwies sich als problematisch. Photooxygenierung in Gegenwart von Ti(OiPr)<sub>4</sub> („Eintopf-Verfahren“) führte zu einem komplexen Produktgemisch, aus dem der Allylalkohol 2c, das Dioxolan 2d und der umgelagerte Epoxyalkohol 2b isoliert werden konnten. Die Struktur des letzteren wurde durch eine Röntgenstrukturanalyse gesichert. Die Behandlung des Allylhydroperoxids 2a mit Ti(OiPr)<sub>4</sub> allein ergab ein ähnlich komplexes Produktgemisch.

As we have recently shown<sup>2)</sup>, the ene reaction of olefins with singlet oxygen in the presence of transition metal catalysts provides a convenient "one-pot" entry into the synthetically valuable epoxy alcohols (Eq. 1). For synthetic purposes it is desirable that as primary step the photooxygen-

ation affords a single hydroperoxide, thus avoiding separation of isomers.

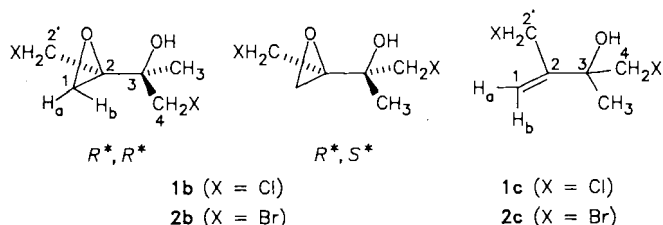
To extend the scope of this reaction, we decided to examine the photooxygenation of symmetrically substituted tetramethylenes and their oxygen transfer behaviour (Eq. 2). In the photooxygenation of the olefins 1–4 ene reaction took place only at the methyl groups, leading to the allylic hydroperoxides 1a–4a. In the <sup>1</sup>H NMR spectra of the crude photooxygenation mixtures no indication of hydrogen abstraction from the CH<sub>2</sub>X groups was detectable. The allylic hydroperoxides were purified by flash chromatography (1a, 2a, 3a) or distillation (4a). The structures were assigned by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (cf. Experimental). The regioselectivity in the photooxygenation of the olefins 1–4, i. e. hydrogen abstraction only from the methyl groups, made them attractive targets for our "one-pot" hydroxyepoxidation. We chose the dihalo-substituted olefins 1 and 2, which should lead to the highly functionalized epoxy alcohols 1b and 2b with the R\*,R\* isomers predominating<sup>2b,3)</sup>.

The photooxygenation of the dichloro olefin 1 in the presence of Ti(OiPr)<sub>4</sub> resulted in the formation of the epoxy alcohol 1b in 78% yield as 77:23 R\*,R\*/R\*,S\* mixture, together with 22% of the allylic alcohol 1c, determined by <sup>1</sup>H NMR (400 MHz) on the crude mixture. Radial chro-

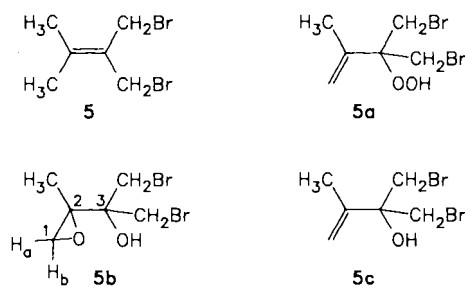


1: X = Cl, 2: X = Br, 3: X = OMe, 4: X = SiMe<sub>3</sub>

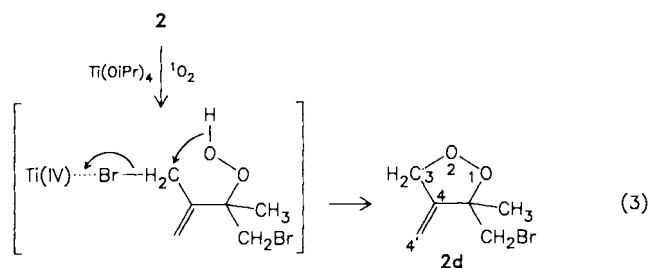
matography on a Chromatotron allowed the isolation of 42% pure  $R^*,R^*$ -**1b** and 9% **1c**, whereas the  $R^*,S^*$ -**1b** diastereomer was no longer detected after chromatography.



In contrast to the dichloro olefin **1**, the photooxygenation of the dibromo olefin **2** in the presence of  $Ti(OiPr)_4$  led to a complex mixture of at least seven products, as confirmed by the number of methyl signals in the  $^1H$  NMR spectrum (400 MHz) of the crude mixture. Three of these products, formed in a ratio of 14:17:69 (normalized to 100%), could be isolated in pure state by chromatography, namely the 1,2-dioxolane **2d** (4%), the allylic alcohol **2c** (4%) and the epoxy alcohol **5b** (12%).



The formation of the 1,2-dioxolane **2d** can be rationalized by nucleophilic attack of the peroxy group in the intermediary allylic hydroperoxide **2a**. The ring closure is facilitated by titanium metal coordination with the bromine (Eq. 3). An authentic sample of the allylic alcohol **2c** was obtained by  $LiAlH_4$  reduction of the allylic hydroperoxide **2a**.



The formation of the epoxy alcohol **5b** was surprising! Small couplings ( $J = 0.7$  Hz) in the  $^1H$  NMR spectrum between the methyl groups and the oxirane protons exclude the expected formation of the epoxy alcohol **2b**, for which in analogy to the chloro-substituted epoxy alcohol **1b** no coupling should be observed. An unambiguous structure proof for **5b** was obtained by X-ray analysis (Figure 1 and Tables 1 and 2).

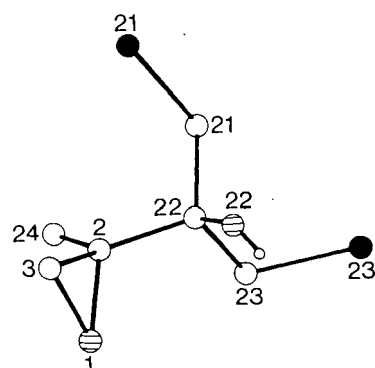


Figure 1. Perspective drawing of the molecular structure of the epoxy alcohol **5b**; the numbering of the atoms corresponds to that of Table 2. White, hatched, and black spheres represent carbon, oxygen, and bromine atoms, respectively

Table 1. X-ray operations and results of the epoxy alcohol **5b**

Crystallographic Section		Data Collection	
empirical formula	$C_6H_{10}Br_2O_2$	diffractometer	Syntax P3
molecular mass	273.96	radiation	MoK $\alpha$
a [pm]	1068.8(7)	monochromator	graphite
b [pm]	1048.2(5)	crystal size [mm]	0.6x0.6x0.25
c [pm]	853.2(5)	data collection mode	$\omega$ -scan
$\beta$ [deg]	110.87(4)	theta range	1.75 - 27.5
V [pm $^3$ ·10 $^{-6}$ ]	893(2)	recip. latt. segment	h = 0 - 13
Z	4		k = 0 - 13
d(calcd) [g·cm $^{-3}$ ]	2.037		l = -11 - 10
crystal system	monoclinic	no. refl. measd.	2279
space group	P2 $_1$ /n	no. unique refl.	2060
		no. refl. F>3 $\sigma$ (F)	1512
		lin. abs. coeff. [cm $^{-1}$ ]	89.35
		abs. correction	$\psi$ -scan
Structural Analysis and Refinement			
solution by	direct phase determination		
method of refinement	anisotropic block diagonal matrix LSQ;		
	H positions were calculated and		
	considered isotropically		
parameter/Fo ratio	0.077		
R, Rw	0.059, 0.046		
program used	SHELXTL (10)		

Table 2. Positional ( $\times 10^4$ ) and thermal [pm $^2 \times 10^{-1}$ ] parameters of the atoms for the epoxy alcohol **5b**. The numbering of the atoms is given in Figure 1; the standard deviations are given in parentheses

	x	y	z	$U_{eq}$
O(1)	803(6)	-903(7)	3684(7)	49(3)
C(2)	2129(8)	-1236(9)	4897(10)	39(4)
C(3)	1953(9)	-188(11)	3710(11)	58(5)
C(21)	3687(9)	-1102(10)	7885(10)	51(4)
Br(21)	4930(1)	-65(1)	7315(1)	61(1)
O(22)	1898(8)	343(7)	6853(9)	44(3)
C(22)	2251(9)	-904(9)	6716(10)	40(4)
C(23)	1277(9)	-1838(9)	7202(10)	51(4)
Br(23)	1230(1)	-1523(1)	9368(1)	77(1)
C(24)	2660(9)	-2494(11)	4623(11)	62(5)

To explain its formation, the following four features have to be considered:

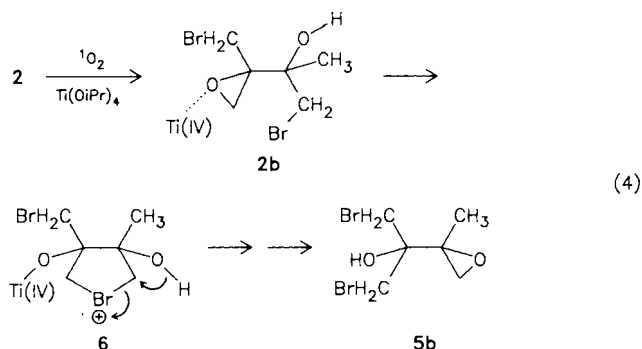
(i) It could be shown that the dibromo regioisomer **5**, which would be a logical precursor for **5b**, was not formed under the photooxygenation or oxygen transfer conditions. Only the  $E$ -**2**  $\rightarrow$   $Z$ -**2** isomerization<sup>4)</sup> could be observed.

(ii) The epoxy alcohol **5b** was also formed together with **2c** and **2d** when the allylic hydroperoxide **2a** was treated with  $\text{Ti}(\text{OiPr})_4$ . Authentic material was prepared by epoxidation of the allylic alcohol **2c** with  $t\text{BuOOH}/\text{Ti}(\text{OiPr})_4$ .<sup>3)</sup> In the latter case the  $^1\text{H}$  NMR spectrum of the crude product showed further signals of low intensity in the typical region of oxirane protons at  $\delta = 2.5\text{--}3.0$ . Unfortunately, it was not possible to show that these signals belong to the epoxy alcohol **2b**, since **2c** was inert towards epoxidation by *m*-chloroperbenzoic acid.

(iii) The addition of a radical inhibitor (5 mol-% of 2,6-di-*tert*-butyl-4-methylphenol) did not prevent the formation of **5b**.

(iv)  $\text{Ti}(\text{OiPr})_4$  caused no isomerization of the allylic alcohol **2c**  $\rightarrow$  **5c**.

On the basis of these facts, the formation of **5b** could derive from isomerization at the allylic hydroperoxide stage, i. e. **2a**  $\rightarrow$  **5a**. While this is possible, there is no rational mechanism nor precedent for such a rearrangement. A more logical alternative is the rearrangement of the expected epoxy alcohol **2b** via a bromonium ion intermediate **6** (Eq. 4). Precedents for such rearrangements are known in the literature<sup>5)</sup>.



Generous financial support by the *Deutsche Forschungsgemeinschaft* (Sonderforschungsbereich Nr. 172, „Molekulare Mechanismen kanzerogener Primärveränderungen“), the *Fritz-Thyssen-Stiftung*, and the *Fonds der Chemischen Industrie* is gratefully appreciated. For spectral services we thank Dr. G. Lange (MS) and Dr. D. Scheutzwow (NMR).

## Experimental

Boiling and melting points are uncorrected, the latter were taken on a Reichert Thermovar Kofler apparatus. — Infrared (IR) spectra: Beckman Acculab 4 and Perkin-Elmer 1420. —  $^1\text{H}$  NMR spectra: Varian EM 390 (90 MHz), Bruker AC 200 (200 MHz), or Bruker WM 400 (400 MHz). —  $^{13}\text{C}$  NMR spectra: Bruker WH 90 (22.6 MHz), Bruker AC 200 (50 MHz), and Bruker WM 400 (100 MHz). — Mass spectra (MS): Varian MAT CH 7. — Combustion analyses: either obtained in-house or from Prof. Maier's staff of the Institute of Organic Chemistry (Gießen). — Thin-layer chromatography (TLC): Polygram SIL G UV (40  $\times$  80 mm), Macherey, Nagel & Co. — Flash chromatography: Silica gel, 32–63  $\mu\text{m}$  (activity I), adsorbent/substrate ratio 50:1, temperature  $-10^\circ\text{C}$ . — Radial chromatography (Chromatotron): Silica gel 60 PF<sub>254</sub> (Merck). — For the photooxygenations a 150-W Phillips G/28/2 sodium lamp with tetraphenylporphyrin (TPP, ca.  $5 \times 10^{-4}$  M) as sensitizer was

used. Stirring was performed magnetically. Commercial reagents and solvents were purchased from standard chemical suppliers and purified to match the reported physical data. The olefins **1**<sup>6)</sup>, **2**<sup>4)</sup>, **3**<sup>7)</sup>, **4**<sup>8)</sup>, and **5**<sup>9)</sup> were prepared according to literature procedures.

**Caution!** The hydroperoxides are potentially dangerous compounds. All safety precautions must be taken.

*X-ray Crystallography of the Epoxy Alcohol 5b*: The special operations and results are listed in Table 1, the positional and thermal parameters in Table 2. The structure is exhibited in Figure 1. Further details of the structure determination are deposited at the Fachinformationszentrum Energie-Physik-Mathematik, 7514 Eggenstein-Leopoldshafen 2 (FRG). These data are available with quotation of the registry number CSD-53087, the authors and the reference of this publication.

*General Procedure for the Photooxygenation of Olefins*: The olefin in  $\text{CH}_2\text{Cl}_2$  (50 ml) was photooxygenated as described in ref.<sup>2d)</sup> at the temperature and time period given below until complete consumption. The solvent was evaporated in a rotary evaporator at  $0^\circ\text{C}$  and 20 Torr, and the crude allylic hydroperoxide was purified by flash chromatography using  $\text{CH}_2\text{Cl}_2$  as eluent for **1a** and **2a** or a 3:5 mixture of methyl *tert*-butyl ether/petroleum ether (30– $50^\circ\text{C}$ ) for **3a** or by distillation for **4a**. The iodometric titer for all hydroperoxides was  $\geq 98\%$ .

*Hydroperoxide 1a*: Starting with 1.10 g (7.19 mmol) of **1**, photooxygenation at  $-10^\circ\text{C}$  for 24 h resulted in 710 mg (53%) of **1a** as a colorless oil. — IR ( $\text{CCl}_4$ ): 3530  $\text{cm}^{-1}$ , 3470, 3110, 3000, 1645, 1455, 1380, 1340, 1280, 1200, 1110, 1090, 940. —  $^1\text{H}$  NMR ( $\text{CCl}_4$ , 90 MHz):  $\delta = 1.50$  (s, 3H,  $\text{CH}_3$ ), AB system ( $\delta_A = 3.89$ ,  $\delta_B = 3.77$ ,  $J = 10.5$  Hz, 2H,  $\text{CH}_2\text{Cl}$ ), 4.20 (s, 2H,  $\text{CH}_2\text{Cl}$ ), 5.37 (s, 1H,  $=\text{CH}_2$ ), 5.56 (s, 1H,  $=\text{CH}_2$ ), 7.83 (s, 1H, OOH). —  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta = 21.09$  (q,  $\text{CH}_3$ ), 43.96 (t), 47.61 (t), 84.88 (s, C–OOH), 119.56 (t,  $=\text{CH}_2$ ), 145.03 (s,  $>\text{C}=\text{}$ ).

$\text{C}_6\text{H}_{10}\text{Cl}_2\text{O}_2$  (185.1) Calcd. C 38.94 H 5.45  
Found C 39.43 H 5.65

*Hydroperoxide 2a*: Starting with 1.10 g (4.54 mmol) of **2**, photooxygenation at  $-10^\circ\text{C}$  for 24 h resulted in 690 mg (55%) of **2a** as a pale yellow oil. — IR ( $\text{CCl}_4$ ): 3530  $\text{cm}^{-1}$ , 3460, 3120, 3000, 1645, 1430, 1380, 1340, 1220, 1105, 1060, 940, 870. —  $^1\text{H}$  NMR ( $\text{CCl}_4$ , 90 MHz):  $\delta = 1.56$  (s, 3H,  $\text{CH}_3$ ), AB system ( $\delta_A = 3.79$ ,  $\delta_B = 3.67$ ,  $J = 10.5$  Hz, 2H,  $\text{CH}_2\text{Br}$ ), 4.12 (s, 2H,  $\text{CH}_2\text{Br}$ ), 5.42 (s, 1H,  $=\text{CH}_2$ ), 5.62 (s, 1H,  $=\text{CH}_2$ ), 8.00 (s, 1H, OOH). —  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta = 23.02$  (q,  $\text{CH}_3$ ), 31.08 (t), 36.90 (t), 84.18 (s, C–OOH), 121.14 (t,  $=\text{CH}_2$ ), 144.96 (s,  $>\text{C}=\text{}$ ).

$\text{C}_6\text{H}_{10}\text{Br}_2\text{O}_2$  (273.9) Calcd. C 26.31 H 3.68  
Found C 26.39 H 3.66

*Hydroperoxide 3a*: Starting with 1.60 g (11.1 mmol) of **3**, photooxygenation at  $-35^\circ\text{C}$  for 24 h afforded 540 mg (28%) of **3a** as a colorless oil. — IR ( $\text{CCl}_4$ ): 3330  $\text{cm}^{-1}$ , 3000, 2950, 2840, 1650, 1460, 1420, 1205, 1100, 940. —  $^1\text{H}$  NMR ( $\text{CCl}_4$ , 90 MHz):  $\delta = 1.30$  (s, 3H,  $\text{CH}_3$ ), 3.35 (s, 3H,  $\text{OCH}_3$ ), 3.40 (s, 3H,  $\text{OCH}_3$ ), 3.48 (d,  $J = 1.5$  Hz, 2H,  $\text{CH}_2\text{OCH}_3$ ), 3.95 (s, 2H,  $\text{CH}_2\text{OCH}_3$ ), 5.27 (s, 2H,  $=\text{CH}_2$ ), 9.30 (s, 1H, OOH). —  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz,  $-20^\circ\text{C}$ ):  $\delta = 20.37$  (q,  $\text{CH}_3$ ), 58.34 (q), 59.53 (q), 73.88 (t), 75.93 (t), 85.37 (s, C–OOH), 120.04 (t,  $=\text{CH}_2$ ), 146.28 (s,  $>\text{C}=\text{}$ ).

*Hydroperoxide 4a*: Starting with 1.50 g (7.00 mmol) of **4**, photooxygenation at  $0^\circ\text{C}$  for 2 h gave 1.46 g (85%) of **4a** as a colorless liquid, b. p.  $72\text{--}75^\circ\text{C}$  at 0.08 Torr. — IR (neat): 3440  $\text{cm}^{-1}$ , 3110, 2960, 2900, 1635, 1420, 1370, 1250, 850, 692. —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta = 0.02$  [s, 9H,  $\text{Si}(\text{CH}_3)_3$ ], 0.08 [s, 9H,  $\text{Si}(\text{CH}_3)_3$ ], 1.05 (s, 2H,  $\text{CH}_2$ ), 1.42 (s, 3H,  $\text{CH}_3$ ), 1.56 (AB System,  $\delta_A = 1.50$ ,  $\delta_B = 1.61$ ,  $J_{AB} = 15.2$  Hz,  $J = 1.0$  Hz,  $J = 0.9$  Hz, 2H,  $=\text{CH}_2$ ), 4.82 (d,

$J = 1.0$  Hz, 1H, =CH<sub>2</sub>), 5.00 (d,  $J = 0.9$  Hz, 1H, =CH<sub>2</sub>), 7.37 (br. s, 1H, OOH, H exchanged with D<sub>2</sub>O). — <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta = -0.5$  (q), 0.3 (q), 20.3 (t), 23.4 (q), 27.1 (t), 87.4 (s), 110.2 (t), 150.3 (s). — MS (70 eV):  $m/z$  (%) = 258 (<1) [M<sup>+</sup> - 2H], 245 (<1) [M<sup>+</sup> - Me], 227 (3) [M<sup>+</sup> - OOH], 147 (15), 141 (8), 123 (4), 115 (8), 75 (37), 73 (100) [SiMe<sub>3</sub>].

C<sub>12</sub>H<sub>28</sub>O<sub>2</sub>Si<sub>2</sub> (260.5) Calcd. C 55.32 H 10.83  
Found C 55.89 H 11.18

**General Procedure for the Photooxygenation of Olefins in the Presence of Ti(OiPr)<sub>4</sub>:** The olefin (1.0 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) was photooxygenated as described in ref.<sup>2d</sup> at 0°C for 24 h in the presence of 1.0 equiv. Ti(OiPr)<sub>4</sub>. The reaction mixture was diluted with ether (100 ml) and water (1 ml per mmol Ti) was added under stirring. After 30 min the precipitate was removed by filtration over Celite, the filtrate dried (MgSO<sub>4</sub>) and evaporated in a rotary evaporator at 20°C and 20 Torr. The residue was purified by radial chromatography on a Chromatotron.

**Photooxygenation of 1 in the Presence of Ti(OiPr)<sub>4</sub>:** According to the general procedure, 3.00 g (19.6 mmol) of **1** and 5.57 g (19.6 mmol) of Ti(OiPr)<sub>4</sub> gave 3.22 g of a 78:22 **1b**:**1c** mixture, the former consisting of R\*,R\*/R\*,S\* diastereomers in a 77:23 ratio, as confirmed by <sup>1</sup>H NMR (400 MHz) of the crude product, integrating the characteristic signals of the oxirane protons at  $\delta = 2.98$  and 3.22 for R\*,R\*-**1b** and at  $\delta = 2.79$  and 2.96 for R\*,S\*-**1b**. Radial chromatography of 500 mg of the crude product using a 1:1 mixture of CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (30–50°C) gave 210 mg (42%) of pure R\*,R\*-**1b** as a colorless oil, which solidified upon cooling. Recrystallization from petroleum ether (30–50°C) yielded colorless prisms, m. p. 63–64°C. As a second fraction 45.0 mg (9%) of **1c** could be isolated as a colorless liquid.

**Epoxy Alcohol (R\*,R\*)-1b:** IR (CDCl<sub>3</sub>): 3570 cm<sup>-1</sup>, 3160, 2980, 1455, 1430, 1375, 1345, 1155, 1130, 1090. — <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 1.47$  (s, 3H, CH<sub>3</sub>), 2.34 (br. s, 1H, OH), 2.98 (d,  $J[1a,1b] = 4.8$  Hz, 1H, 1a-H), 3.22 (dd,  $J[1b,1a] = 4.8$  Hz,  $J[1b,2'b] = 0.8$  Hz, 1H, 1b-H), 3.61 (d,  $J[2'a,2'b] = 12.5$  Hz, 1H, 2'a-H), AB system ( $\delta_A = 3.68$ ,  $\delta_B = 3.73$   $J[A,B] = 11.6$  Hz, 4a-, 4b-H), 3.93 (dd,  $J[2'b,2'a] = 12.5$  Hz,  $J[2'b,1b] = 0.8$  Hz, 1H, 2'b-H). — <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 23.2$  (q), 43.9 (t), 50.3 (t), 50.4 (t), 71.8 (s), 77.9 (s). — MS (70 eV):  $m/z$  (%) = 171 (0.3), 169 (0.5), 121 (4), 119 (13), 99 (54), 93 (27), 77 (10), 69 (10), 57 (57), 43 (100). C<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>2</sub> (185.1) Calcd. C 38.94 H 5.45  
Found C 38.62 H 5.45

**Allylic Alcohol 1c:** IR (CCl<sub>4</sub>): 3590 cm<sup>-1</sup>, 3100, 2980, 2940, 1425, 1375, 1330, 1260, 1095, 1045. — <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 1.50$  (s, 3H, CH<sub>3</sub>), 2.60 (br. s, 1H, OH), AB system ( $\delta_A = 3.61$ ,  $\delta_B = 3.78$ ,  $J[A,B] = 10.4$  Hz, 4a-, 4b-H), AB system ( $\delta_A = 4.17$ ,  $\delta_B = 4.21$ ,  $J[A,B] = 12.3$  Hz,  $J[2'a,1b] = J[2'b,1b] = 0.9$  Hz, 2'a-, 2'b-H), 5.42 (s, 1H, 1a-H), 5.46 (dd,  $J[1b,2'a] = J[1b,2'b] = 0.9$  Hz, 1H, 1b-H). — <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 26.3$  (q), 44.2 (t), 53.5 (t), 74.0 (s), 117.6 (t), 147.7 (s). — MS (70 eV):  $m/z$  (%) = 135 (4) [M<sup>+</sup> - <sup>37</sup>Cl], 133 (8) [M<sup>+</sup> - <sup>35</sup>Cl], 121 (5), 119 (16), 93 (11), 85 (16), 77 (17), 69 (8), 57 (17), 43 (100).

C<sub>6</sub>H<sub>10</sub>Cl<sub>2</sub>O (169.1) Calcd. C 42.63 H 5.97  
Found C 42.32 H 6.13

**Photooxygenation of 2 in the Presence of Ti(OiPr)<sub>4</sub>:** According to the general procedure, 3.00 g (12.4 mmol) of **2** and 3.52 g (12.4 mmol) of Ti(OiPr)<sub>4</sub> resulted in 2.80 g of a complex mixture of products (at least seven compounds detected by TLC). Radial chromatography of 1.00 g of the crude product eluting with a 1:1 mixture of CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (30–50°C) gave 39 mg (4%) of **2d** and 42 mg (4%) of **2c** as colorless liquids and 120 mg (12%) of **5b**

as a pale yellow oil, which solidified upon cooling. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (30–50°C) afforded colorless prisms, m. p. 64–66°C, which were used for X-ray structure determination.

**1,2-Dioxolane 2d:** IR (CDCl<sub>3</sub>): 3090 cm<sup>-1</sup>, 2990, 2910, 2870, 1670, 1370, 1240, 1180, 1060, 970. — <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 1.50$  (s, 3H, CH<sub>3</sub>), 3.33 and 3.60 (d,  $J = 11.0$  Hz, 2H, CH<sub>2</sub>Br), AB system ( $\delta_A = 4.65$ ,  $\delta_B = 4.70$ ,  $J[A,B] = 9.3$  Hz,  $J = 2.3$  Hz, 3-H), 5.05 and 5.13 (ddd,  $J = 2.3$  and 2.3 Hz,  $J = 1.2$  Hz, 2H, 4'-H). — <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 20.7$  (q), 37.1 (t), 73.4 (t), 84.1 (s), 105.5 (t), 154.9 (s). — MS (70 eV):  $m/z$  (%) = 194 (0.2) [M<sup>+</sup>], 192 (0.2) [M<sup>+</sup>], 179 (2), 177 (2), 139 (3), 137 (3), 99 (66), 95 (25), 84 (3), 43 (100). C<sub>6</sub>H<sub>9</sub>BrO<sub>2</sub> (193.0) Calcd. C 37.33 H 4.70  
Found C 37.56 H 4.90

**Allylic Alcohol 2c:** IR (CDCl<sub>3</sub>): 3560 cm<sup>-1</sup>, 3100, 2980, 2915, 1600, 1450, 1420, 1215, 1080, 1045. — <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta = 1.57$  (s, 3H, CH<sub>3</sub>), 2.42 (br. s, 1H, OH), AB system ( $\delta_A = 3.59$ ,  $\delta_B = 3.74$ ,  $J[A,B] = 10.5$  Hz, 4-H), 4.11 (s, 2H, 2'-H), 5.41 and 5.50 (s, 2H, 1-H). — <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta = 27.2$  (q), 31.5 (t), 44.3 (t), 73.6 (s), 119.0 (t), 148.0 (s). — MS (70 eV):  $m/z$  (%) = 179 (2) [M<sup>+</sup> - <sup>81</sup>Br], 177 (2) [M<sup>+</sup> - <sup>79</sup>Br], 165 (1), 163 (1), 139 (2), 137 (2), 99 (65), 95 (29), 67 (16), 43 (100).

C<sub>6</sub>H<sub>10</sub>Br<sub>2</sub>O (258.0) Calcd. C 27.94 H 3.91  
Found C 28.10 H 3.86

**Epoxy Alcohol 5b:** IR (CDCl<sub>3</sub>): 3540 cm<sup>-1</sup>, 3070, 2980, 2930, 2860, 1435, 1345, 1235, 1025, 860. — <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta = 1.48$  (d,  $J[CH_3,1a] = 0.7$  Hz, 3H, CH<sub>3</sub>), 2.61 (d,  $J[1b,1a] = 4.7$  Hz, 1H, 1b-H), 2.72 (br. s, 1H, OH), 3.05 (dq,  $J[1a,1b] = 4.7$  Hz,  $J[1a,CH_3] = 0.7$  Hz, 1H, 1a-H), AB system ( $\delta_A = 3.53$ ,  $\delta_B = 3.68$ ,  $J[A,B] = 11.0$  Hz, CH<sub>2</sub>Br), AB system ( $\delta_A = 3.65$ ,  $\delta_B = 3.74$ ,  $J[A,B] = 11.0$  Hz, CH<sub>2</sub>Br). — <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta = 18.0$  (q), 36.3 (t), 37.5 (t), 50.7 (t), 58.8 (s), 71.7 (s). — MS (70 eV):  $m/z$  (%) = 219 (4), 217 (8), 215 (4), 181 (8), 179 (8), 138 (24), 136 (24), 121 (16), 57 (75), 43 (100).

C<sub>6</sub>H<sub>10</sub>Br<sub>2</sub>O<sub>2</sub> (274.0) Calcd. C 26.31 H 3.68  
Found C 26.41 H 3.49

The X-ray data of **5b** are given in Tables 1 and 2 and the structure is exhibited in Figure 1.

**Reaction of 2a with Ti(OiPr)<sub>4</sub>:** At 0°C 520 mg (1.82 mmol) of Ti(OiPr)<sub>4</sub> was added to 500 mg (1.82 mmol) of **2a** in CH<sub>2</sub>Cl<sub>2</sub> (5 ml), and the mixture was stirred for 12 h. Workup according to the general procedure resulted in a product mixture, that showed the same signals in the <sup>1</sup>H NMR spectrum (200 MHz) as those of the product mixture obtained in the "one-pot" procedure for the functionalization of **2**.

**Sharpless Epoxidation of 2c with tert-BuOOH/Ti(OiPr)<sub>4</sub>:** At 0°C 1.00 ml (3.00 mmol) of tert-BuOOH (3.0 M in CH<sub>2</sub>Cl<sub>2</sub>) was added to 258 mg (1.00 mmol) of **2c** and 284 mg (1.00 mmol) of Ti(OiPr)<sub>4</sub>, and the mixture was stored for 12 h in a refrigerator. Removal of Ti(OiPr)<sub>4</sub> as described in the general procedure afforded 410 mg of crude product that consisted of a 90:10 mixture of **5b** and an unknown compound, besides tert-butyl alcohol and tert-butyl hydroperoxide.

**Reduction of 2a by LiAlH<sub>4</sub>:** A sample of 2.82 g (10.3 mmol) of crude **2a** in ether (10 ml) was added at -78°C to 190 mg (5.00 mmol) of LiAlH<sub>4</sub> in ether (50 ml) and stirred for 2 h, the temperature slowly being raised to 0°C. Cautious addition of water (0.4 ml), 2 N NaOH (0.4 ml) and water (1.2 ml) resulted in the formation of a white precipitate, which was removed by filtration. The filtrate was dried (MgSO<sub>4</sub>) and evaporated in a rotary evaporator at 0°C and 20 Torr to give 2.04 g (70%) of **2c**, which was used without further purification in the above epoxidation.

## CAS Registry Numbers

(E)-1: 1587-31-1 / 1a: 115384-24-2 / (R\*,R\*)-1b: 115384-28-6 / (R\*,S\*)-1b: 115384-30-0 / 1c: 115384-32-2 / (E)-2: 6044-73-1 / 2a: 115384-25-3 / 2c: 115384-33-3 / 2d: 115384-29-7 / (E)-3: 115406-82-1 / 3a: 115384-26-4 / (E)-4: 16054-38-9 / 4a: 115384-27-5 / 5b: 115384-31-1

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