Regio- and Diastereoselective Synthesis of Stannyl Epoxy Alcohols by Direct Hydroxy Epoxidation of Vinylstannanes

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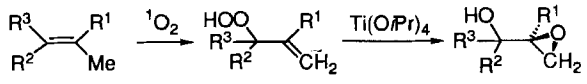
The direct synthesis of stannyl epoxy alcohols **3** from vinylstannanes **1** is described. The procedure involves the photooxygenation of vinylstannanes **1**, which proceeds in a highly regioselective manner with predominant hydrogen abstraction geminal to the stannyl group. Subsequent reaction of the resulting hydroperoxides **2** with $Ti(OiPr)_4$ afforded in a one-pot procedure the epoxy alcohols **3** in high diastereomeric excess, which ranged from 81:19 to greater than 95:5. This convenient and effective method was applied to acyclic and cyclic vinylstannanes as well as to γ-hydroxyvinylstannane **1e**, which was converted into the stannyl epoxy diol **3e**. In this novel hydroxy epoxidation of vinylstannanes the regioselectivity of the singlet oxygen ene reaction (Schenck reaction) is controlled by the stannyl group.

The photooxygenation of olefins in the presence of transition metal catalysts, the hydroxy epoxidation[1] of alkenes, has been shown to be a powerful method for the stereoselective synthesis of epoxy alcohols. Thereby, allylic hydroperoxides are formed by the singlet oxygen ene reaction (Schenck reaction), as shown in eq. (1), which are subsequently converted by the action of epoxidation catalysts like $Ti(OiPr)_4$ or $VO(acac)_2$ into the corresponding epoxy alcohols. If stereogenic centers are present in the olefin, e.g. as in chiral allylic alcohols[2], further stereocontrol can be obtained, and up to three additional stereogenic centers can be introduced in a defined manner by means of one synthetic operation.



(1)

Application of this procedure to simple alkenes, however, often gives rise to mixtures of epoxy alcohols since the photooxygenation step may proceed with low regioselectivity to yield isomeric hydroperoxides. This drawback has recently been overcome by the application of the hydroxy epoxidation procedure to vinylsilanes[3], which react with singlet oxygen with high *gem* selectivity[4]. In view of the bulkiness of the silyl group, the stereoselectivity of the epoxidation step is additionally increased.

Recently, it has been shown that also vinylstannanes[5] react in a highly regio- and stereoselective manner with singlet oxygen to yield the corresponding β-stannyl-allylic hydroperoxides with high regioselectivity. Thus, it was of interest to assess whether the hydroxy epoxidation procedure could also be extended to vinylstannanes. In this way stannylated epoxy alcohols would become conveniently accessible, a class of compounds which so far has received little attention[6]. In the following we present our results, which show that the direct hydroxy epoxidation of vinylstannanes proceeds regio- and diastereoselectively to afford stannylated epoxy alcohols with a wide range of substitution patterns.

Results

The required vinylstannanes **1** were prepared by standard procedures[5] in one or two steps from cheap and readily available starting materials. Derivative **1a**[7] was obtained as a 77:23 mixture of *Z*/*E* isomers from commercial 2-bromo-2-butene and the corresponding Grignard reagent. Stannylation of 1-lithio-1-cyclohexene[8], derived from 1-chloro-1-cyclohexene, afforded derivative **1d**. Reductive lithiation of the corresponding vinyl thioether[5] was the source of vinylstannane **1b**, whereas **1c** was available from cyclopentanone by employing the Shapiro reaction[5,9]. The γ-hydroxyvinylstannane **1e** was synthesized from the corresponding propargylic alcohol by hydromagnesation and subsequent stannylation[10,11].

Attempts to convert the vinylstannanes **1** directly into the epoxy alcohols **3** by the literature one-step procedure[1,4] failed. This method consists of the photooxygenation of these substrates in the presence of titanium isopropoxide. At the temperature (−20°C) at which the vinylstannanes **1** are converted into the thermally labile, intermediary hydroperoxides, almost no conversion to the epoxy alcohols **3** was observed. Additionally, it is difficult to exclude rigorously adventitious water in the low-temperature photooxygenation and, consequently, hydrolysis of the titanium catalyst under these conditions becomes unavoidable.

These problems could be circumvented by applying a one-pot but two-step procedure. Thus, after photooxygenation of the vinylstannanes **1** in dichloromethane, the crude reaction mixture was dried with molecular sieves and sub-

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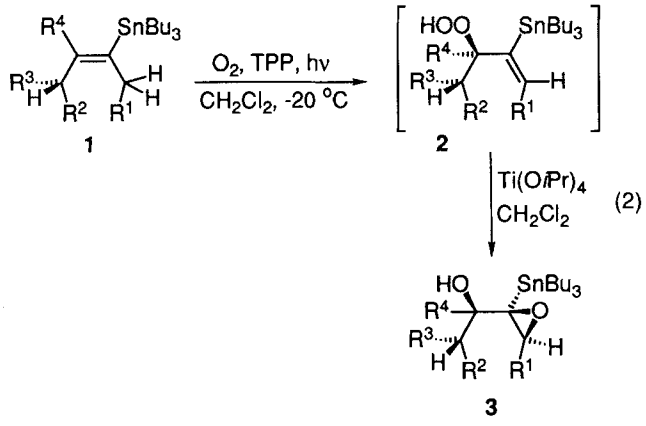
sequently the titanium isopropoxide (12–67 mol%) was added at 0°C (eq.2). The results are summarized in Table 1.



(2)

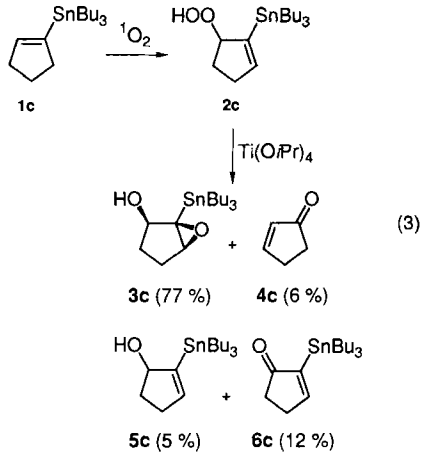
Table 1. Hydroxy epoxidation of vinylstannanes **1a–e**

	Vinylstannane 1				Reaction time [h]		Stannyl epoxy alcohol 3	
	R^1	R^2	R^3	R^4	t_1[a]	t_2[b]	yield [%]	d. r.[c]
1a	H	H	H	H	7	15	40	81 : 19
1b	H	H	H	Me	2	6	54	–
1c	CH_2		H	H	1.2	16	55	> 95 : 5
1d	$[CH_2]_2$		H	H	7.5	15	24	> 95 : 5
1e	H	Me	OH	H	4	0.25	50	> 95 : 5

[a] Photooxygenation time in CH_2Cl_2 with tetraphenylporphine (TPP) as sensitizer, 2 × 150-W sodium lamps, except **1d**, for which 2 × 250-W sodium lamps were used. – [b] Run at 0°C with 50–67 mol% of Ti(O*i*Pr)$_4$, except **1e**, for which conditions were 20°C and 12 mol% of Ti(O*i*Pr)$_4$. – [c] *erythro*:*threo* ratio.

For the complete conversion of the hydroperoxides **2a–d**, reaction times in the range 6–16 h were necessary at 0°C, whereas derivative **2e** was consumed already within 15 min at 20°C. Hydrolysis and workup afforded diastereomeric mixtures of the stannylated epoxy alcohols **3** in moderate overall yields (24–55%) after flash chromatography on silica gel. For all substrates high diastereomeric ratios (d.r.) were obtained, with the *erythro* product **3** being the major isomer. The designation *erythro* refers to the relative configuration of the hydroxy and the epoxy functionalities. For **3a**, the *erythro* selectivity was 81:19, but for the cyclic **1c,d** and the stannyl epoxy diol **3e** it was > 95:5.

The hydroxy epoxidation of **1** was examined in detail by analysis of the crude reaction mixtures directly by NMR spectroscopy, as displayed for derivative **1c** in eq. (3). Besides the stannyl epoxy alcohols **3** as the main product, also the enones **4** were detected as byproducts (< 10%), which were identified by a comparison with authenic samples[11,12,13]. These enones result from the regioisomeric ene products obtained in the photooxygenation by loss of stannyl hydroxide[5]. Additionally, always about 5% of the reduction products **5** were detected. In fact, in the case of **1e**, as much as 30% of the *threo* stannyl diol **5e**[11] was found, which was isolated in 24% yield by flash chromatography (eq.4). For **1c,d** also the corresponding α-stannyl enones **6c,d**[13] (eq.3) were formed in 12 and 22% yield, respectively. The latter result from the dehydration of the intermediary hydroperoxides **2**.



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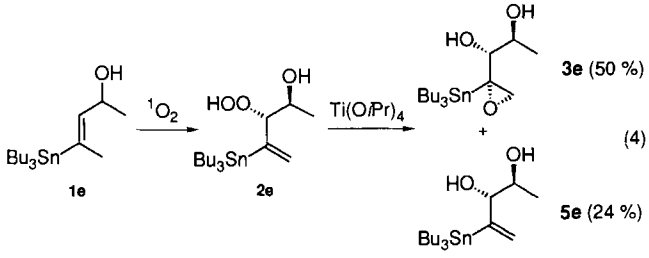


(4)

An authenic sample of **3a** was obtained as a 38:62 mixture of (R^*,R^*) and (R^*,S^*) isomers by the epoxidation of the alcohol **5a** with *m*-chloroperbenzoic acid.

The structural assignment of the stannyl epoxy alcohols **3** is based on the comparison with the analogous silylated[3] or methyl-substituted[1] epoxy alcohols. Thus, the ^{1}H-NMR signal of the hydrogen α to the OH group in the stannyl epoxy alcohol (R^*,R^*)-**3a** is located at lower field than for the *threo* (R^*,S^*) isomer, as displayed by the other *erythro* isomers. Additionally, the signals of the epoxy protons constitute a well-separated set of doublets for the *erythro* but a narrow set for the *threo* isomers.

The single isomers of the cyclic derivatives **3c,d** were assigned the *cis* configuration, since in dilute CCl_4 solution they displayed intramolecular hydrogen bonds[14] in their IR spectra. A large coupling constant of the hydroxy protons with the hydrogens α to the OH group, which was also detected in the corresponding silylated epoxy alcohols, supports this assignment and speaks for a rigid conformation of the hydroxy group. In view of the small $J_{2,3}$ value, which is characteristic[2] of such epoxy diols, the *erythro* stereochemistry, i.e. the (2S^*, 3R^*, 4R^*) configuration, was also assigned to the epoxy diol **3e**.

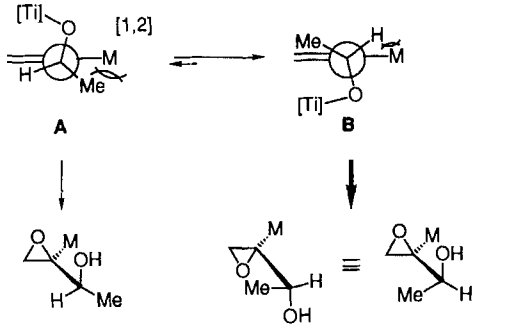
Discussion

The established *gem*-directing effect of the stannyl group[5] makes possible the regioselective synthesis of β-stannylallylic hydroperoxides **2**, especially for cyclic vinylstannanes or for substrates with a methyl group in the geminal position. The low amounts of regioisomeric ene prod-

uct, which are formed in the singlet oxygen ene reaction (Schenck reaction), do not give rise to regioisomeric epoxy alcohols, as is the case with alkyl-substituted olefins. The regioisomeric hydroperoxides decompose in situ during the photooxygenation to the α,β-enones **4**, which do not interfere in the epoxidation process.

The high diastereomeric ratios obtained in the direct hydroxy epoxidation of vinylstannanes with $Ti(OiPr)_4$ are in good agreement with the generally accepted mechanism of metal-catalyzed epoxidation of allylic alcohols[15]. The *erythro* diastereoselectivity in the hydroxy epoxidation of substrate **1a** (d.r. = 81:19) is somewhat lower than for the other derivatives, but mechanistically more significant is the fact that the d.r. value is also lower than for the corresponding silyl analogues (d.r. = 93:7)[3] and about the same as for the methyl derivative (d.r. = 83:17)[1a]. This trend can be rationalized in terms of the dihedral angle C=C−C−O of 100°, which was proposed for the titanium-catalyzed epoxidations[1] (Scheme 1). In the two possible conformers **A** and **B**, the degree of diastereoselectivity is determined by the 1,2-allylic strain between the carbinyl group and the metal substituent (M). This interaction is lower for conformer **B** and, thus, the oxygen transfer mainly affords the *erythro* epoxy alcohol. However, the effective steric bulk of the stannyl group[16] is substantially lower than that of the silyl group, due to the longer carbon-tin bond (Scheme 1) so that the steric differentiation in the stannylated system is lower than in the silylated one and comparable to the methyl-substituted case.

Scheme 1



M	r_{C-M} [pm]	erythro : threo
Me	154	83 :17
$SiMe_3$	187	93 : 7
$SnBu_3$	215	81 :19

For **1e**, the Schenck reaction proceeds with complete regiocontrol and high *threo* selectivity[11] to form the (S^*,R^*)-hydroperoxy homoallylic alcohol **2e** in a 95:5 ratio (eq.4). Clearly, the cooperative effects exercised by the *gem*-directing regioselectivity of the stannyl group and the *threo*-controlling diastereoselectivity of the chiral allylic alcohol functionality are evident. The subsequent oxygen transfer step also occurs with high stereoselectivity, which has been established for the alkyl-substituted analogues[2]. Thus, starting from **1e**, we have introduced the two new stereogenic centers in a completely stereoselective manner with ($2S^*$, $3R^*$, $4R^*$)-**3e** as single isomer.

In contrast to the Sharpless-type epoxidation of allylic diols with *tert*-butyl hydroperoxide, which is known to be extremely sluggish[17], the titanium-catalyzed oxygen transfer process reported in this paper is complete within 15 min for **1e**. This advantage is attributed to the nature of the oxygen donor involved in this hydroxy epoxidation[2]. Thus, the hydroperoxy homoallylic alcohol **2e** (eq.4), which acts as a tridentate oxygen donor, can displace by ligand exchange the tridentate epoxidation product **3e** at the titanium metal center much more effectively than the bidentate *tert*-butyl hydroperoxide and regenerate the so-called loaded titanium complex, i.e. simultaneous ligation of the oxygen donor (hydroperoxide) and oxygen acceptor (allylic alcohol) occurs at the metal center[2]. Thus, the catalytic cycle for oxygen transfer operates effectively with low amounts of $Ti(OiPr)_4$ (12%) even for epoxy diol **3e**.

Generally, the epoxidation step involved in the syntheses described in this paper is somewhat slower than for the comparable silyl-[3] and methyl-substituted[1] systems. This is especially significant for the methyl analogue of substrate **1e**, which is efficiently epoxidized also below 0°C within minutes[2], whereas the hydroperoxy alcohol **2e** requires 15 min at 20°C in the epoxidation step for full conversion. This trend coincides with the larger amounts of byproducts produced in the epoxidation process of **1d** and **1e**. Especially the larger amount of reduction product **5e** (eq.4), presumably formed by an Oppenauer-type oxidation of the coordinated isopropoxy ligand at the titanium metal in the reactive complex[1a], is indicative of slow epoxidation as normally found in the hydroxy epoxidation of electron-deficient alkenes[1]. Since the epoxidation step constitutes an electrophilic attack on the double bond system, this implies that vinylstannanes should be more electron-deficient than alkyl- or silyl-substituted olefins. That this is, indeed, the case is shown by photoelectron spectroscopy of vinyl substrates[18], since tributylvinylstannane displays a higher π-type ionization potential (10.0 eV) than vinylsilanes (9.8 eV) or monosubstituted alkenes (9.7−9.9 eV).

In summary, it has been shown that the one-pot but two-step procedure described in this paper represents a valuable method for the synthesis of stannylated epoxy alcohols. Although the yields are only moderate over the two reaction steps, the starting materials are readily available, and the oxy functionalization is convenient. Additionally, the high stereocontrol cannot be achieved by peracid or dioxirane epoxidations of the corresponding allylic alcohols, as shown in the *m*CPBA epoxidation of allylic alcohol **5a**. Moreover, the preparation of the epoxy diol **3e** by metal-catalyzed epoxidation of the diol **5e** with *tert*-butyl hydroperoxide should be ineffective in view of the well-established low reactivity of allylic diols under Sharpless-type conditions[17]. Thus, the present methodology constitutes a valuable route for the preparation of these highly oxy-functionalized organotin derivatives.

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vierter Moleküle). P. K. thanks the *Fonds der Chemischen Industrie* for a doctoral fellowship (1992–1994).

Experimental

IR: Perkin-Elmer, 1420. – ^{1}H NMR: Bruker AC 200 (200 MHz), $CDCl_3$ (δ = 7.26) as internal standard. – ^{13}C NMR: Bruker AC 200 (50 MHz), $CDCl_3$ (δ = 77.0) as internal standard. – CH_2Cl_2 was purified by filtration over basic alumina (activity grade I). $Ti(OiPr)_4$ was distilled and stored under argon. The vinylstannanes **1a–d**[5] and **1e**[10,11] were synthesized as previously reported. 3-(Tributylstannyl)-3-buten-2-ol (**5a**)[12] and 4-(tributylstannyl)-4-pentene-2,3-diol (**5e**)[11] were prepared by photooxygenation of **1a** or **1e** and subsequent reduction of the hydroperoxide with $NaBH_4$ or triphenylphosphane. For photooxygenations the reported experimental setup was used[5,11].

General Procedure for the Hydroxy Epoxidation of Vinylstannanes **1a–d**: A solution of 2.80–5.79 mmol of **1** and 20 mg of tetraphenylporphine (TPP) in 50 ml of dichloromethane was placed into a 100-ml Schlenk tube and cooled to −20°C. The photooxygenation was conducted by continuously passing a slow stream of dried oxygen gas ($CaCl_2$, silica gel, P_4O_{10}) through the solution by means of a disposable pipette and external irradiation with two 150-W sodium lamps (for **1d** two 250-W sodium lamps) until complete consumption of the starting material (TLC monitoring). The exact experimental conditions are given in Table 1. To the crude photooxygenate was added 1 g of molecular sieves (4 Å) at 0°C, and the mixture was well stirred for 10 min. Subsequently, 50–67 mol % of $Ti(OiPr)_4$ was added, and the mixture was stirred at 0°C for 6–16 h. The molecular sieves were removed from the reaction mixture and washed with ether (5 × 2 ml). Ether (30 ml) and water [1 ml per mmol of $Ti(OiPr)_4$] were added to the combined organic layers, and the mixture was stirred at 20°C for 2 h. The solution was filtered over Celite, dried ($MgSO_4$), and concentrated (0°C at 20 Torr). Flash chromatography on silica gel (50 g) gave the epoxy alcohols **2**, which eluted considerably slower than the byproducts.

α-Methyl-2-(tributylstannyl)-2-oxiranemethanol (**3a**): According to the above procedure 2.00 g (5.79 mmol) of vinylstannane **1a** (*Z*:*E* = 77:23) was photooxygenated for 7 h. Stirring with 820 mg (2.90 mmol, 50%) of $Ti(OiPr)_4$ for 15 h, workup, and flash chromatography on silica gel [eluent: petroleum ether (30–50°C)/ether (5:1)] afforded 870 mg (2.31 mmol, 40%) of a colorless oil, (*R**,*R**)-**3a**:(*R**,*S**)-**3a** = 81:19. – IR (neat): $\tilde{\nu}$ = 3600–3100 cm^{-1} (OH), 3005, 2940, 2905, 2850, 2835, 1450, 1408, 1370, 1339, 1284, 1243, 1070, 928, 874, 699, 642. – $C_{16}H_{34}O_2Sn$ (377.2): calcd. C 50.95, H 9.09; found C 51.27, H 9.38.

(*R**,*R**)-**3a**: ^{1}H NMR ($CDCl_3$): δ = 0.75–1.12 (m, 15H, $SnBu_3$), 1.17 (d, *J* = 6.4 Hz, 3H, CH_3), 1.22–1.70 (m, 12H, $SnBu_3$), 2.16 (d, *J* = 1.3 Hz, 1H, OH), 2.53 (d, *J* = 4.9 Hz, 1H, CH_2), 2.90 (d, *J* = 4.9 Hz, 1H, CH_2), 3.96 (qd, *J* = 6.5/1.3 Hz, 1H, C*H*OH). – ^{13}C NMR ($CDCl_3$): δ = 9.0 (t), 13.6 (q), 19.0 (q), 27.4 (t), 29.0 (t), 46.2 (t), 59.9 (s), 69.0 (d).

(*R**,*S**)-**3a**: ^{1}H NMR ($CDCl_3$): δ = 0.75–1.12 (m, 15H, $SnBu_3$), 1.18 (d, *J* = 6.6 Hz, 3H, CH_3), 1.22–1.70 (m, 12H, $SnBu_3$), 2.23 (br s, 1H, OH), 2.67 (m, 2H, CH_2), 3.32 (q, *J* = 6.6 Hz, 1H, C*H*OH). – ^{13}C NMR ($CDCl_3$): δ = 9.5 (t), 13.6 (q), 19.9 (q), 27.4 (t), 29.0 (t), 48.4 (t), 62.8 (s), 75.7 (d).

α,α-Dimethyl-2-(tributylstannyl)-2-oxiranemethanol (**3b**): According to the above procedure 1.50 g (4.18 mmol) of vinylstannane **1b** was photooxygenated for 2 h. Stirring with 793 mg (2.79 mmol, 67%) of $Ti(OiPr)_4$ for 6 h, workup, and flash chromatography on silica gel [eluent: petroleum ether (30–50°C)/ether (4:1)] afforded 887 mg (2.27 mmol, 54%) of a violet oil, R_f = 0.34, which contained traces of TPP. – IR (neat): $\tilde{\nu}$ = 3600–3180 cm^{-1} (OH), 2930, 2900, 2840, 2820, 1445, 1361, 1350, 1327, 1170, 1140, 1062, 949, 900, 840. – ^{1}H NMR ($CDCl_3$): δ = 0.75–1.10 (m, 15H, $SnBu_3$), 1.13 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.20–1.70 (m, 12H, $SnBu_3$), 2.08 (s, 1H, OH), 2.51 (d, *J* = 4.9 Hz, 1H, CH_2), 2.88 (d, *J* = 4.9 Hz, 1H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 9.8 (t), 13.6 (q), 25.0 (q), 27.4 (t), 28.9 (t), 29.2 (q), 47.1 (t), 63.5 (s), 71.8 (s). – $C_{17}H_{36}O_2Sn$ (391.2): calcd. C 52.20, H 9.28; found C 52.37, H 9.27.

(1α,2β,5β)-1-(Tributylstannyl)-6-oxabicyclo[3.1.0]hexan-2-ol (**3c**): According to the above procedure 1.00 g (2.80 mmol) of vinylstannane **1c** was photooxygenated for 70 min. Stirring with 400 mg (1.40 mmol, 50%) of $Ti(OiPr)_4$ for 16 h, workup, and flash chromatography on silica gel [eluent: petroleum ether (30–50°C)/ether (4:1)] afforded 603 mg (1.55 mmol, 55%) of a violet oil, which contained traces of TPP. – IR (CCl_4): $\tilde{\nu}$ = 3560 cm^{-1} (OH), 2935, 2900, 2845, 2825, 1448, 1367, 1351, 1055, 875, 665. – ^{1}H NMR ($CDCl_3$): δ = 0.75–1.08 (m, 15H, $SnBu_3$), 1.08–1.70 (m, 14H, $SnBu_3$, CH_2), 1.73 (d, *J* = 10.6 Hz, 1H, OH), 1.78–1.90 (m, 1H, CH_2), 2.17 (m, 1H, CH_2), 3.30 (br s, 1H, CH), 4.02 (dt, *J* = 10.5/7.9 Hz, 1H, C*H*OH). – ^{13}C NMR ($CDCl_3$): δ = 8.9 (t), 13.6 (q), 26.9 (t), 27.0 (t), 27.3 (t), 29.0 (t), 59.3 (d), 64.8 (s), 79.3 (d). – $C_{17}H_{34}O_2Sn$ (389.2): calcd. C 52.47, H 8.81; found C 52.55, H 9.11.

(1α,2β,6β)-1-(Tributylstannyl)-7-oxabicyclo[4.1.0]heptan-2-ol (**3d**): According to the above procedure 2.00 g (5.39 mmol) of vinylstannane **1d** was photooxygenated for 7.5 h. Stirring with 766 mg (2.70 mmol, 50%) of $Ti(OiPr)_4$ for 15 h, workup, and flash chromatograhy on silica gel [eluent: petroleum ether (30–50°C)/ether (4:1)] afforded 534 mg (1.32 mmol, 24%) of a colorless oil, R_f = 0.50. – IR (CCl_4): $\tilde{\nu}$ = 3560 cm^{-1} (OH), 2930, 2900, 2845, 2825, 1449, 1441, 1367, 1071, 1025, 879, 685, 650. – ^{1}H NMR ($CDCl_3$): δ = 0.75–1.15 (m, 15H, $SnBu_3$), 1.15–1.70 (m, 16H, $SnBu_3$, CH_2), 1.70–2.05 (m, 2H, CH_2), 1.80 (d, *J* = 10.0 Hz, 1H, OH), 3.20 (d, *J* = 3.4 Hz, 1H, CH), 3.80 (ddd, *J* = 10.0/7.9/4.9 Hz, 1H, C*H*OH). – ^{13}C NMR ($CDCl_3$): δ = 9.0 (t), 13.7 (q), 19.1 (t), 23.7 (t), 27.4 (t), 29.0 (t), 29.1 (t), 59.0 (d), 63.4 (s), 72.7 (d). – $C_{18}H_{36}O_2Sn$ (403.2): calcd. C 53.62, H 9.00; found C 54.00, H 9.34.

(2S,3R*,4R*)-4,5-Epoxy-4-(tributylstannyl)-2,3-pentanediol* (**3e**): According to the above procedure 870 mg (2.32 mmol) of vinylstannane **1e** was photooxygenated for 4 h. The crude photooxygenate was dried over 0.5 g of molecular sieves at 0°C. After the addition of 79.0 mg (278 μmol, 12 mol %) of $Ti(OiPr)_4$ at 0°C, the solution was stirred for 15 min at 20°C. The molecular sieves were removed and washed with ether (5 × 2 ml). The combined organic layers were stirred with 0.5 ml of water for 1.5 h, and the solvent was removed by rotoevaporation (0°C at 20 Torr). Flash chromatography of the residue on silica gel [eluent: petroleum ether (30–50°C)/ether (1:1)] afforded 518 mg (1.27 mmol, 50%) of **3e** as a violet oil (traces of TPP), and 216 mg (552 μmol) of the corresponding stannyl diol (*S**,*R**)-**5e**[11].

(2*S**,3*R**,4*R**)-**3e**: IR (neat): $\tilde{\nu}$ = 3620–3100 cm^{-1} (OH), 2995, 2960, 2900, 2880, 1469, 1088, 1061, 880. – ^{1}H NMR ($CDCl_3$): δ = 0.70–1.15 (m, 15H, $SnBu_3$), 1.23 (d, *J* = 6.5 Hz, 3H, CH_3), 1.15–1.70 (m, 12H, $SnBu_3$), 2.49 (d, *J* = 4.5 Hz, 1H, OH), 2.70 (d, *J* = 6.8 Hz, 1H, OH), 2.72 (d, *J* = 4.3 Hz, 1H, CH_2), 2.88 (d, *J* = 4.4 Hz, 1H, CH_2), 3.42 (dd, *J* = 6.7/2.4 Hz, 1H, C*H*OH), 3.73 (qdd, *J* = 6.4/4.5/2.4 Hz, 1H, C*H*OH). – ^{13}C NMR ($CDCl_3$): δ = 9.5 (t), 13.6 (q), 19.6 (q), 27.4 (t), 29.0 (t), 48.0 (t), 60.6 (s), 66.7 (d), 77.4 (d). – $C_{17}H_{36}O_3Sn$ (407.2): calcd. C 50.15, H 8.91; found C 50.55, H 9.36.

(*S**,*R**)-**5e**: IR (neat): $\tilde{\nu}$ = 3640–3080 cm^{-1} (OH), 3030, 2950, 2920, 2860, 2840, 1453, 1410, 1370, 1260, 1120, 1069, 1030, 923, 665. – ^{1}H NMR ($CDCl_3$): δ = 0.70–1.15 (m, 15H, $SnBu_3$), 1.33

(d, J = 6.3 Hz, 3H, CH_3), 1.15–1.70 (m, 12H, $SnBu_3$), 2.38 (d, J = 3.2 Hz, 1H, OH), 2.43 (d, J = 3.5 Hz, 1H, OH), 3.59 (dqd, J = 7.0/6.3/3.5 Hz, 1H, C*H*OH), 3.91 (br dd, J = 7.0/3.2 Hz, 1H, C*H*OH), 5.34 (dd, J = 2.2/1.0, J_{HSn} = 60.6 Hz, 1H, =CH), 5.88 (dd, J = 2.3/1.2, J_{HSn} = 125/133 Hz, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 10.1 (t), 13.7 (q), 18.8 (q), 27.4 (t), 29.0 (t), 70.0 (d), 84.5 (d), 127.5 (t), 155.6 (s). – $C_{17}H_{36}O_2Sn$ (391.2): calcd. C 52.20, H 9.28; found C 52.62, H 9.78.

Epoxy Alcohol **3a** *by mCPBA Epoxidation of 3-(Tributylstannyl)-3-buten-2-ol:* 361 mg (1.00 mmol) of 3-(tributylstannyl)-3-buten-2-ol[12] was dissolved in 20 ml of CH_2Cl_2 and 0.50 g of solid $NaHCO_3$ was subsequently added to the solution. At 0°C a solution of 296 mg (1.20 mmol) of *m*-chloroperbenzoic acid in 10 ml of CH_2Cl_2 was added, and the mixture was stirred for 5 h. It was then washed with water (20 ml), a satd. $NaSO_3$ and a satd. $NaHCO_3$ solution (3 × 20 ml), dried ($MgSO_4$), and concentrated (20°C/20 Torr). Flash chromatography of the residue on 50 g of silica gel [eluent: petroleum ether (50–60°C)/ether (4:1)] gave 177 mg (469 μmol, 47%) of a colorless oil, (*R**,*R**):(*R**,*S**)-**3a** = 38:62.

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