Hydroxy-Directed Regio- and Diastereoselective Ene Reaction of Singlet Oxygen with Chiral Allylic Alcohols

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Abstract: The photooxygenation of chiral allylic alcohols **1a**, (*Z*)-**1f–k**, ethers **1b–d**, and acetate **1e** gave the corresponding hydroperoxy homoallylic alcohols and derivatives **2** through the ene reaction with singlet oxygen. While the reaction of the acetate **1e** proceeded *erythro*-diastereoselectively as a result of the classical *cis* effect, for the allylic alcohols **1a** and (*Z*)-**1f–k**, in which an alkyl group is located *cis* to the hydroxy-bearing substituent, high *threo* selectivity was observed. This finding is explained in terms of coordination of the nucleophilic hydroxy functionality of the stereogenic center with the incoming electrophilic singlet oxygen enophile. The stereodifferentiation is a consequence of the preferred conformation of the allylic alcohol for oxygen transfer, which is mainly determined by 1,3-allylic strain, while the influence of 1,2-allylic strain is small. A similar sensitivity toward both types of allylic strain is observed in epoxidations with *m*-CPBA, for which stereocontrol by cooperation of hydroxy-coordination and allylic strain is established. These similarities were convincingly demonstrated for the chiral allylic alcohol (*Z*)-**1g** as a novel stereochemical probe. Moreover, from these results it can be concluded that the optimal C=C—C—O dihedral angle of the allylic alcohol in the transition state for the singlet oxygen ene reaction lies between 90° and 130°. In addition to the *threo* selectivity with which the hydroperoxy moiety is introduced, the newly formed allylic double bond in the hydroperoxide is exclusively formed in the *E* configuration, as exemplified for the chiral allylic alcohol (*Z*)-**1k**; again, allylic strain in the $^1O_2$ ene reaction is responsible.

The prototropic ene reaction of singlet oxygen ($^1O_2$) with alkenes represents a convenient route to allylic hydroperoxides, a class of compounds of versatile synthetic utility.[1] Much effort has been invested to achieve regio- and diastereocontrol in this prototropic ene reaction, and the by now classical *cis* effect[2] constitutes one of the prominent factors of attaining this goal with some success. More recently, the *gem*-directing effect[3] and the "nonbonding large group" interactions[4] have been recognized. Additionally, excellent regiocontrol is exercised by silyl[4b,5] substituents on the double bond, which direct oxyfunctionalization to the α-allylic site. Furthermore, although diastereofacial differentiation in cyclic and bicyclic substrates has been abundantly documented in $^1O_2$ ene reactions,[6] for acyclic olefins such control was only recently accomplished.[2c,d] Again, it is the *cis* effect[2] which provides the opportunity for diastereomeric selection.

Previously we reported[7] that the photooxygenation of chiral allylic alcohols proceeds with a high degree of regio- and diastereoselectivity which was attributed to coordination of the hydroxy functionality with the incoming $^1O_2$. Such directing effects, which are well-recognized in peracid[8] and transition metal-catalyzed[8c,d,9] epoxidations as well as in nitrile oxide cycloadditions,[10] were hitherto unknown for $^1O_2$ reactions. Herewith we report the full details on the synthetic and mechanistic features of this useful regio- and diastereoselectively controlled $^1O_2$ ene reaction.

Results

Photooxygenation of the allylic alcohols **1a**, (*Z*)-**1f–k**, and (*E*)-**1f,g**, ethers **1b–d**, and the acetate **1e** afforded the corresponding β-hydroperoxy homoallylic alcohols and derivatives **2** as a result of the ene reaction with singlet oxygen (Scheme I). The observed product ratios, which were determined by ^1H NMR spectroscopy directly on the crude reaction mixture after evaporation of the solvent, are given in Tables I and II.

The conversion of the allylic alcohols **1a** and (*Z*)-**1f–k**, which bear an alkyl substituent *cis* to the hydroxy group, proceeded with high regio- and diastereoselectivity to afford predominantly the *threo*-configurated hydroperoxides (*S**,*S**)-**2a,f–k** (entries 1 and 8–13, Table I). The degree of *threo* selectivity for these allylic alcohols is, within error limits, independent of the alkyl substituents

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Scheme I
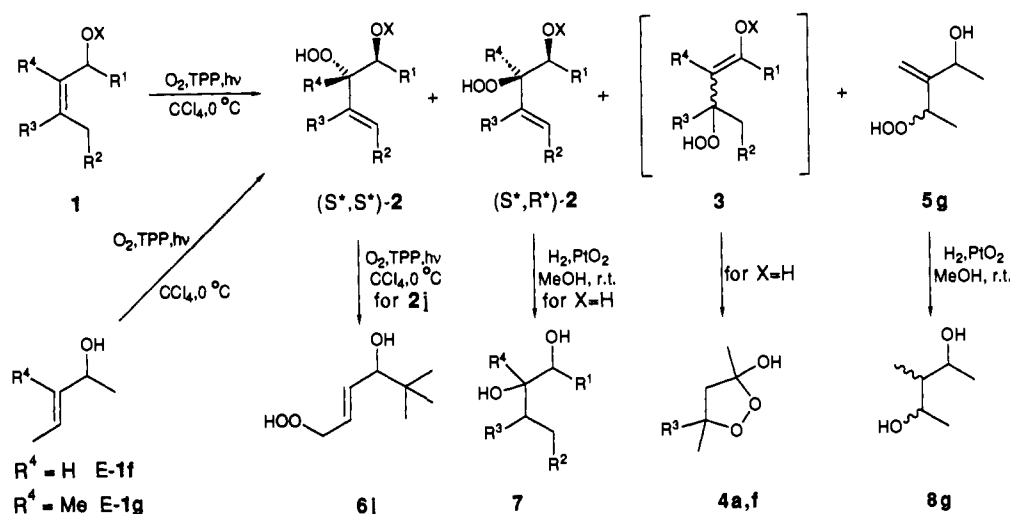
Table I: Regio- and Diastereoselectivity^a in the Photooxygenation of Chiral Allylic Alcohols **1a**, (*Z*)-**1f–k**, Ethers **1b–d**, and Acetate **1e**

		R^1	R^2	R^3	R^4	X	solvent	diastereoselectivity		regioselectivity	
								(S*,S*)-2	(S*,R*)-2	2	3
1	**1a**	Me	H	Me	H	H	CCl$_4$	93	7	96	4^b
2	**1a**	Me	H	Me	H	H	MeOH^c	73	27	96	4^b
3	**1a**	Me	H	Me	H	H	MeCN^c	76	24	96	4^b
4	**1b**	Me	H	Me	H	SiMe$_3$	CCl$_4$	80	20	74	26^d
5	**1c**	Me	H	Me	H	SiMe$_2$-*t*-Bu	CCl$_4$	83	17	67	33^d
6	**1d**	Me	H	Me	H	Me	CCl$_4$	72	28	80	20^d
7	**1e**	Me	H	Me	H	Ac	CCl$_4$	39	61	82	18^e
8	(*Z*)-**1f**	Me	H	H	H	H	CCl$_4$	93	7	>97	<3^f
9	(*Z*)-**1g**	Me	H	H	Me	H	CCl$_4$	93	7	>97	<3^{f,g}
10	(*Z*)-**1h**	Et	H	H	H	H	CCl$_4$	94	6	>97	<3^f
11	(*Z*)-**1i**	*i*-Pr	H	H	H	H	CCl$_4$	94	6	>97	<3^f
12	(*Z*)-**1j**	*t*-Bu	H	H	H	H	CCl$_4$^{h}	95	5	>97	<3^f
13	(*Z*)-**1k**	Me	*n*-Pr	H	H	H	CCl$_4$	94	6^i	>97	<3^f

^{a} Error was ±5% of stated value. ^{b} The regioisomer **3a** was observed in the form of its ring tautomer **4a**. ^{c} Rose bengal was used as sensitizer. ^{d} The intermediary enol ethers **3b–d** were unstable under the reaction conditions. ^{e} (*E*)-**3e**:(*Z*)-**3e** = 38:62. ^{f} No products **3f–k** could be detected. ^{g} 8% of [(S*,S*),(S*,R*)]-**5** was formed as side products in a 23:77 ratio. ^{h} The photooxygenation was conducted in the presence of 10 mol % 2,6-di-*tert*-butyl-4-methylphenol as radical scavenger. ^{i} Only *E*-configurated hydroperoxides **2k** were detected.

Table II: Regio- and Diastereoselectivity^a in the Photooxygenation of Chiral Allylic Alcohols (*E*)-**1f,g**

		R^4	solvent	diastereoselectivity		regioselectivity	
				(S*,S*)-2	(S*,R*)-2	2	3
1	(*E*)-**1f**	H	CCl$_4$	54	46	96	4^b
2	(*E*)-**1g**	Me	CCl$_4$	66	34	>97	<3^{b,c}

^{a} Error was ±5% of stated value. ^{b} The regioisomer **3f** was observed in the form of its ring tautomer **4f**. ^{c} 45% of [(S*,S*),(S*,R*)]-**5** was formed as side products in a 66:34 ratio.

located in the *cis* position [Me as in **1a**, (*Z*)-**1f–j** and *n*-Pr as in (*Z*)-**1k**] and at the stereogenic unit [R^1 = Me as in **1a**, (*Z*)-**1f,g**; Et as in (*Z*)-**1h**; *i*-Pr as in (*Z*)-**1i**; and *t*-Bu as in (*Z*)-**1j**]. In the case of (*Z*)-**1k**, additional to the large *threo* selectivity, the new double bond is selectively introduced to give exclusively *E*-configurated hydroperoxide **2k** (entry 13, Table I). On the contrary, the extent of stereoselection was rather low for the allylic alcohols (*E*)-**1f,g** which lack such a *cis* substituent (Table II). A methyl group located in the *gem* position to the hydroxy-bearing substituent has only a small influence on the stereochemical course of the reaction (entries 8 and 9, Table I; entry 2, Table II). While the conversion of the allylic alcohol (*E*)-**1g** proceeded in low selectivity (entry 2, Table II), the degree of diastereoselection for (*Z*)-**1f** and (*Z*)-**1g**, the latter additionally possessing a *gem* methyl group, is high and identical (entries 8 and 9, Table I).

Furthermore, (*Z*)-**1g** was allowed to react with *m*-CPBA and VO(acac)$_2$/*t*-BuOOH.[11] In the peracid epoxidation high *threo* diastereoselectivity was observed, whereas the vanadium-catalyzed

reaction proceeded *erythro*-selectively (eq 1). In the photo-

	threo-**10**	*erythro*-**10**
m-CPBA	90	10
VO(acac)$_2$/*t*-BuOOH	33	67
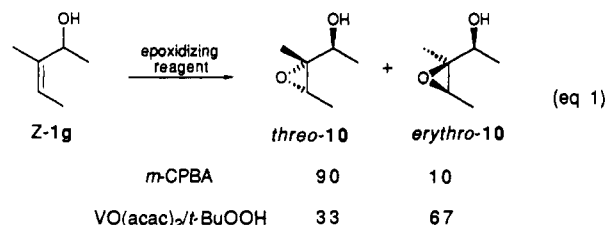
oxygenations of **1a** and (*E*)-**1f** the dioxolanes **4a,f** were detected in minor amounts, which arise from ketonization of the initial enols **3a,f** followed by cyclization.[12] Moreover, in the photooxygenation of allylic alcohols (*E*)- and (*Z*)-**1g** the diastereomeric hydroperoxides (S*,S*)- and (S*,R*)-**5g** were formed as regioisomeric side products.

The degree of stereoselection depends on the solvent in which the photooxygenation is performed. As demonstrated for allylic alcohol **1a**, for example, in methanol and acetonitrile significantly lower stereoselectivities were obtained than in CCl$_4$ (entries 1–3, Table I). Compared to the allylic alcohol **1a**, the corresponding allylic ethers **1b–d** gave smaller selectivities (cf. entries 1 versus 4–6, Table I). Furthermore, in the latter photooxygenations

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several unidentified products were formed, presumably by subsequent reactions of the intermediary enol ethers **3b–d** with singlet oxygen;[3d,6d] the latter result from regioisomeric photo-oxygenation.

An opposite sense of stereocontrol was observed in the ene reaction of the allylic acetate **1e**, for which the *erythro*-configurated hydroperoxide (*S**,*R**)-**2e** dominates (entry 7, Table I). In this case the regioisomeric products (*Z*,*E*)-**3e** also were detected in a ratio which is within error limits identical to that of (*S**,*R**)- and (*S**,*S**)-**2e**.

Control experiments, i.e. irradiation of allylic alcohols **1a–k** in the absence of sensitizer and prolonged photooxygenation of the corresponding hyroperoxides, established that, except for derivative **2j**, all starting materials and products were stable under the reaction conditions. In the case of **2j**, rearrangement[13] to the terminal hydroperoxide **6j** was observed (Scheme I), which could be suppressed by addition of 2,6-di-*tert*-butyl-4-methylphenol as radical scavenger.

Diastereomeric Assignments

The relative configurations of **2a,f–h,k** and **5g** were determined by chemical correlation through catalytic reduction to the corresponding literature-known[14] saturated diols **7a,f–h,k** and **8g** (Scheme I). For hydroperoxide **2k** the large coupling constant[15] of the olefinic protons (J = 15.5 Hz) establishes the *E* configuration of the double bond. Desilylation of the silyl ether **2b** by silica gel in methanol at room temperature (9 h) gave allylic hydroperoxide **2a**, which allowed assessment of the relative configuration of **2b**.

The stereochemistry of the acetate **2e** was established by conversion to the diol **9a** by LiAlH₄ reduction (eq 2). The latter

(eq 2)
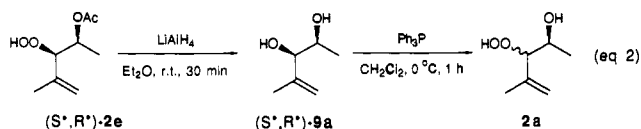
was alternatively prepared by Ph₃P treatment of the allylic hydroperoxide **2a** (eq 2). The configurational assignment of the diastereomeric enol acetates **3e** is based on the fact[16] that the olefinic proton of (*E*)-**3e** (δ = 5.20) is shifted downfield relative to the *Z*-isomer (*Z*)-**3e** (δ = 5.11). More convincingly, irradiation of the allylic methyl protons of (*Z*)-**3e** at δ = 1.90 gave a significant NOE enhancement (1.2%) of the olefinic proton at δ = 5.11.

All secondary allylic hydroperoxides **2** displayed similar spectral characteristics: (a) the resonances of both OC*H* protons of the *S**,*S** hydroperoxides are shifted upfield relative to the *S**,*R** isomers, (b) the vicinal coupling constants of these protons are higher for (*S**,*S**)-**2** versus (*S**,*R**)-**2**, (c) the signals of the hydroxy-bearing carbon atoms are shifted downfield for (*S**,*S**)-**2** relative to their *S**,*R**-configurated counterparts, and (d) with the exception of **2j**, the latter trend is also observed for the resonances of the carbon atoms which carry the hydroperoxy functionality. On the basis of these spectral criteria and the

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(15) Günther, G. *NMR Spektroskopie*; Thieme Verlag: Stuttgart, 1992; Chapter 4. Additionally, for derivative [*S**,*S**-(*E*)]-**2k** this assignment was confirmed by an NOE experiment.

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Scheme II
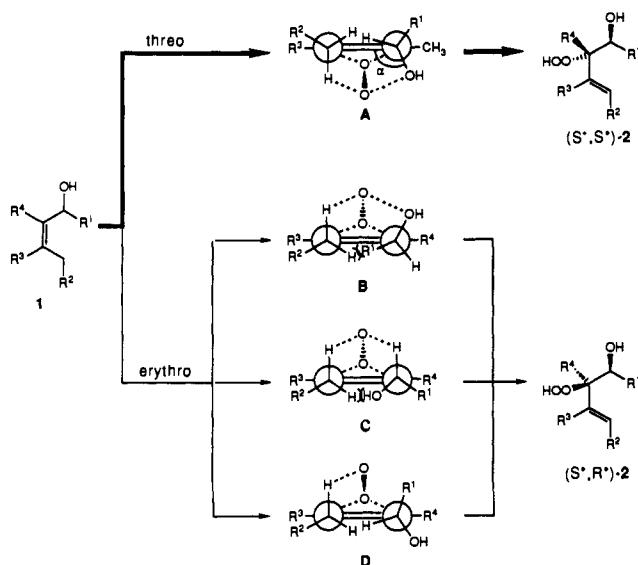
chemical correlation of **2a,b,e–h,k**, the stereochemistry of **2c,d,i,j** was assessed.

The stereochemistry of the epoxy alcohols **10** was assigned by comparison of the ¹H NMR spectra with known examples.[17] Thus, for the diastereomeric epoxy alcohols the carbinol proton of the *erythro* isomer (δ = 3.77) is generally observed at lower field than the corresponding proton of the *threo* isomer (δ = 3.69).

Discussion

The above results provide compelling evidence that the ene reaction of singlet oxygen with allylic alcohols is governed by an interaction between the enophile ¹O₂ and the allylic hydroxy functionality of the chiral alcohol. The stereodifferentiation is then a consequence of the preferred conformation of the allylic alcohol in the transition state (the C=C—C—O dihedral angle should be of the order of 90–130°), which is determined predominantly by 1,3-allylic strain[18] (Scheme II). Side products may arise from competing ene reactions without involvement of the allylic HO group. Experimental features which are in favor of this mechanism include the following:

(a) *The classical cis effect*[2] *is not operating in the ene reactions of the chiral allylic alcohols* **1a** *and* (*Z*)-**1f–k**. Had a *cis* effect[2] operated, the enophilic attack of ¹O₂ would be for optimal intramolecular assistance directed to that side of the substrate which aligns two allylic hydrogens perpendicular to the olefin plane to flank the terminal perepoxide oxygen. Of the two possible geometries for the transition states which fulfill this condition, namely *threo-* versus *erythro*-A*, the *threo*-A* arrangement should be destabilized due to severe 1,3-allylic strain due to methyl–methyl interactions (Scheme III). As a consequence, the photooxygenation would be expected to proceed mainly through the *erythro*-A* transition state and, thus, the *erythro*-configurated hydroperoxides (*S**,*R**)-**2** should dominate. Instead, the preferred formation of the *threo* hydroperoxides suggests that the stereochemical course of this ene reaction is efficiently controlled by a mechanism not subject to the classical *cis* effect.[2]

(b) *The presence of a free HO group is essential to achieve high degrees of selectivity.* That the allylic hydroxy functionality is directly involved is inferred from the solvent dependence on the diastereoselectivity, as exemplified for allylic alcohol **1a** (entries 1–3, Table I). In methanol and acetonitrile, solvents which can

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Scheme III
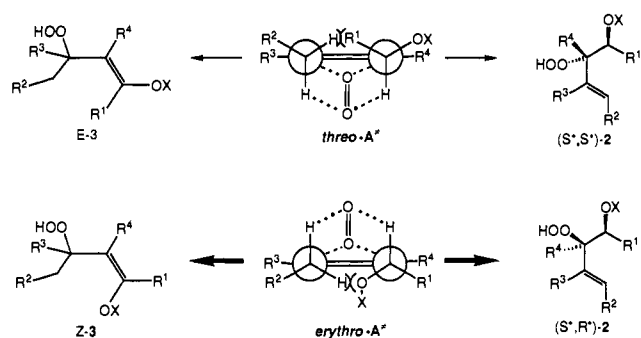
interact with the HO group by hydrogen bonding, a significant drop in the diastereoselectivity is observed. Moreover, functionalization of the HO group also leads to decreased selectivity. While the allylic ethers **1b–d** still react with appreciable *threo* selectivity (entries 4–6, Table I), for the acetate **1e** an inverted sense of diastereoselection is observed, i.e. the *erythro*-configurated hydroperoxide (S^*,R^*)-**2e** dominates (entry 7, Table I); thus, for the acetate the classical *cis* effect[2] operates. This happenstance is further substantiated by the fact that the regioisomeric ene products, i.e. the enol acetates (Z,E)-**3e**, are formed with the same diastereomeric ratio (dr) value as the *gem*-selective $[(S^*,R^*), (S^*,S^*)]$-**2e** regioisomers. Therefore, both sets of regioisomers must each derive from a common precursor, namely *erythro*-A[*] for the major diastereomers (S^*,R^*)-**2e**, (Z)-**3e** and *threo*-A[*] for the minor (S^*,S^*)-**2e**, (E)-**3e** (X = OAc, Scheme III).

From these substituent effects the nature of the directing effect of the HO group can be inferred. In view of the electrophilic properties[19] of $^1O_2$, it is reasonable to assume that for the alcohols **1a** and (Z)-**1f–k**, as well as the ethers **1b–d**, the nucleophilic allylic oxygen functionalities of these substrates initially interact with the electrophilic $^1O_2$ thereby directing the attack of this enophile mainly to give the *threo*-configurated products. In the case of the corresponding acetate **1e**, the less nucleophilic oxygen functionality at the chiral allylic position does not interact as effectively with $^1O_2$; hence, the reaction is governed by the classical *cis* effect[2] and *erythro* selectivity is preferred.

The controlling action of the ether functionalities is smaller than that of the HO group, as indicated by the reduced degree of *threo* selectivity in the conversions of derivatives **1b–d** (entries 4–6, Table I) compared to that of the free alcohol **1a** (entry 1, Table I). This may derive from steric hindrance by the silyl and methyl substituents which hinders the approach of $^1O_2$ to the allylic oxygen so that the classical *cis* effect[2] may compete.

Our results imply that during the early stage of the photooxygenation, i.e. during exciplex formation, but well before the perepoxide transition state is reached, the HO group interacts through its nucleophilic oxygen atom with the electrophilic $^1O_2$. Once this diastereofacial control has occurred, the HO group can then through hydrogen bonding interact with the negatively charged terminal oxygen atom of the subsequently formed perepoxide transition state and further stabilize the aggregate; however, the stereoselective control appears to derive from the initial interaction between the electrophilic $^1O_2$ and the nucleophilic oxygen atom of the HO group in the exciplex.

(c) *1,3-Allylic strain[18] is responsible for the threo diastereoselectivity.* If one accepts the premise that the enophilic attack of $^1O_2$ is directed by the allylic hydroxy functionality, the stereochemical differentiation is then a consequence of the preferred conformation of the hydroxy group of the chiral allylic alcohol in the transition state of the ene reaction. Thus, the diastereoselectivity presumably originates from allylic strain[18] by substituents at the double bond. The importance of such 1,3-

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allylic strain[18] caused by a substituent *cis* to the hydroxy-bearing substituent is recognized by comparison of the photooxygenations of the chiral allylic alcohols **1a**, (Z)-**1f**, and (E)-**1f,g** (compare entries 1 and 8, Table I *versus* entries 1 and 2, Table II). The absence of a methyl group *cis* to the hydroxy-bearing substituent in derivative (E)-**1f** would suggest little 1,3-allylic strain, and consequently almost complete loss of diastereoselectivity is observed (entry 1, Table II). On the other hand, the presence of an additional methyl group in the *gem* position, which introduces 1,2-allylic strain, causes only a minor effect as best revealed by the very similar stereoselectivities observed in the photooxygenation of derivatives (Z)-**1f,g** (entries 8 and 9, Table I) and (E)-**1f,g** (entries 1 and 2, Table II).

(d) *The C=C—C—O dihedral angle of the allylic alcohol in the transition state of the $^1O_2$ ene reaction is of the order of ca. 90–130°.* Control of stereoselectivity by cooperation of hydroxy-coordination and allylic strain is well-established for epoxidations of allylic alcohols with *m*-CPBA and VO(acac)$_2$/*t*-BuOOH (Table III). Nevertheless, both reactions exhibit a different sensitivity toward 1,2- and 1,3-allylic strain,[18] which is explained in terms of the proposed[8d–f,9] transition-state geometries *threo*-1[*] and *erythro*-1[*]. While for *m*-CPBA epoxidations a C=C—C—O

threo-1[*]
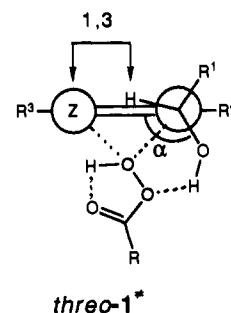
preferred transition state
for *m*-CPBA epoxidations
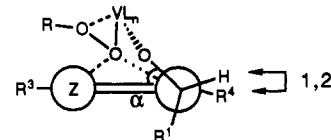
erythro-1[*]

preferred transition state for
vanadium-catalyzed epoxidations

dihedral angle of ca. 120° appears to be optimal,[8d] for the vanadium-catalyzed reaction an angle of ca. 50° applies.[8d] Dominating control through 1,3-allylic strain[18] accounts for the results in the former (compare entries 1 and 2 with 4 for *m*-CPBA, Table III) and 1,2-allylic strain[18] in the latter (compare entries 1 and 2 with 3 for VO(acac)$_2$/*t*-BuOOH, Table III). These differences are most convincingly demonstrated in the epoxidations of (Z)-**1g** (eq 1; entry 6, Table III), a substrate which serves as a versatile stereochemical probe[11] since it has the advantage of possessing both a *cis* methyl group (Z = Me) for 1,3-allylic strain and a *gem* methyl group (R^4 = Me) for 1,2-allylic strain and thus allows assessment of the relative importance of such steric interactions.

As expected on the basis of coordination by the hydroxy group and allylic strain, the *m*-CPBA epoxidation of (Z)-**1g** exhibits a high degree of *threo* diastereoselectivity due to 1,3-allylic interactions, while the vanadium-catalyzed reaction proceeds

Table III: Stereoselectivities in the Epoxidations and Singlet Oxygen Ene Reactions of Chiral Allylic Alcohols **1** (X = H)

| | | Z^a | R^3 | R^4 | strain[b] | *threo/erythro* selectivity | | |
| | | | | | | epoxidation | | ene reaction |
						m-CPBA	VO(acac)$_2$/tBuOOH	$^1O_2$
1		H	H	H		60:40[c]	20:80[c]	
2	(*E*)-**1f**	H	Me	H		64:36[c]	29:71[c]	54:46[d]
3		H	H	Me	1,2	45:55[c]	5:95[c]	
4	(*Z*)-**1f**	Me	H	H	1,3	95:5[c]	71:29[c]	93:7[e]
5	**1a**	Me	Me	H	1,3	95:5[c]	86:14[c]	93:7[e]
6	(*Z*)-**1g**	Me	H	Me	1,2 + 1,3	90:10[f]	33:67[f]	93:7[e]

[a] Z = CH$_2$R^2 in structure **1** of Scheme I. [b] Type of allylic strain involved in the diastereoselectivity. [c] Values from ref **8d**. [d] Cf. Table II. [e] Cf. Table I. [f] Cf. eq 1.

Scheme IV
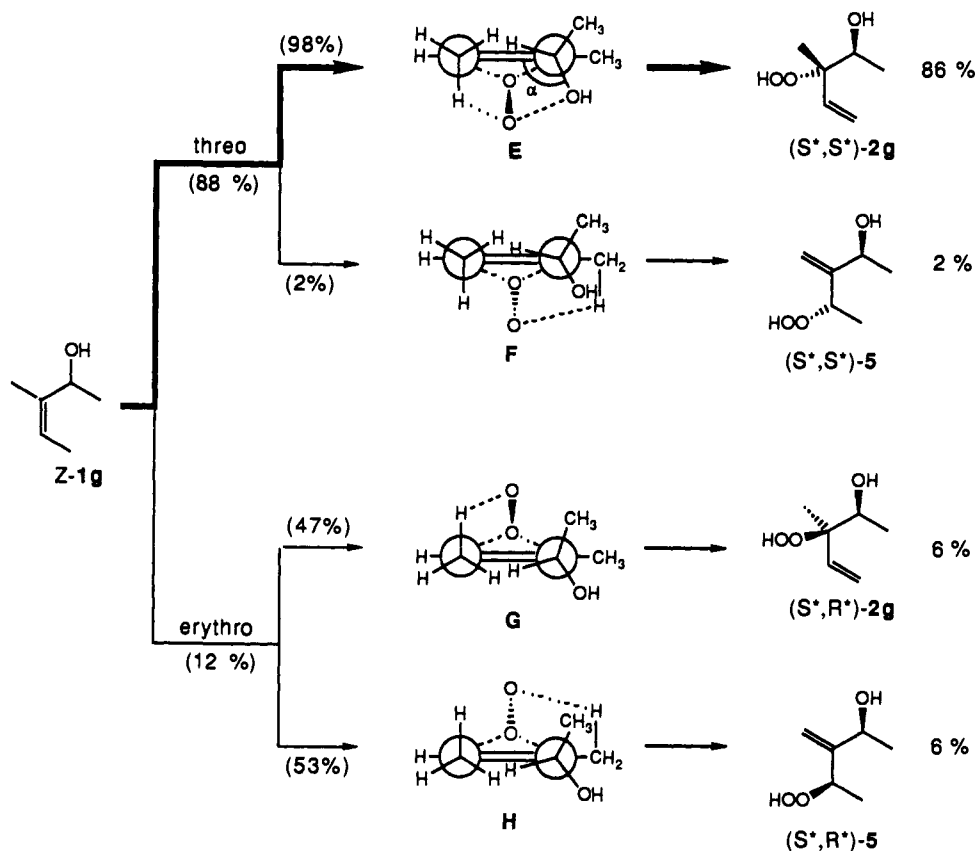
erythro-selectively due to control by 1,2-allylic strain. Nonetheless, that 1,3-allylic interactions can be important for VO-(acac)$_2$/*t*-BuOOH epoxidations is reflected in the small degree of *erythro* diastereoselection in the epoxidation of (*Z*)-**1g**. This is also evident for **1a** and (*Z*)-**1f** as substrates, in which 1,2-allylic strain is small while 1,3-allylic strain becomes more significant (entries 4 and 5 for VO(acac)$_2$/*t*-BuOOH, Table III). Similarly, the slight reduction in the *threo* selectivity for the *m*-CPBA epoxidations of 3-methyl-3-buten-2-ol and (*Z*)-**1g** (entries 3 and 6 for *m*-CPBA, Table III) derives presumably from increased 1,2-allylic strain.

At this point a comparison of the stereochemical course of the singlet oxygen ene reaction with the *m*-CPBA and vanadium-catalyzed epoxidations is instructive. As can be seen in Table III, not only the sense but also the extent of diastereoselection of the singlet oxygen ene reaction and the *m*-CPBA epoxidation are very similar, i.e. *threo* control, whereas large differences are evident for the vanadium-catalyzed epoxidation. The oxidations of our stereochemical probe (*Z*)-**1g** (entry 6, Table III), for which the stereochemical course is affected by *1,2- and 1,3-allylic strain*,[18] especially underline these differences. These results imply that the singlet oxygen ene reaction is subject to 1,2- and 1,3-

allylic strain in the same manner as the *m*-CPBA epoxidation; hence, the preferred transition-state geometries of the allylic alcohols must be very similar. Since the optimal C=C—C—O dihedral angle (α) in the transition state for the *m*-CPBA epoxidation[8d] is ca. 120°, it follows that for the singlet oxygen ene reaction α should lie between 90° and 130° (structure A, Scheme II).

(e) *Ene reactions without participation of the HO group may compete.* To a minor extent singlet oxygen may react with allylic alcohols by alternative pathways, similar to reactions of unfunctionalized olefins, i.e. without involvement of the allylic HO group. The formation of the hydroperoxides **5g** in the photooxygenation of (*Z*)-**1g** demonstrates this possibility hydrogen abstraction from the *gem* methyl group cannot be assisted by coordination with the HO group because of lack of proximity (structures F and H, Scheme IV). In this context, the high regioselectivity which results from *threo* attack to afford the allylic hydroperoxides (*S**,*S**)-**2g** and (*S**,*S**)-**5g** in a ratio of 98:2 is remarkable and accentuates the importance of the directing effect of the hydroxy functionality. On the other hand, *erythro* attack involves rather unselective hydrogen abstraction [(*S**,*R**)-**2g**:(*S**,*R**)-**5g** = 47:53], which confirms that for both *erythro* diastereomers (*S**,*R**)-**2g** and

Scheme V
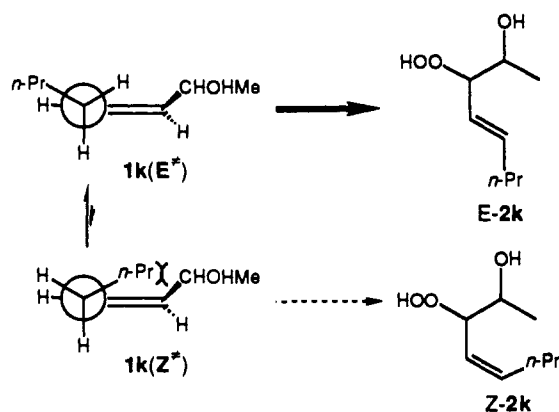
(*S*,R**)-**5g** control by the hydroxy group is not operating since otherwise (*S*,R**)-**2g** should have been preferentially formed relative to (*S*,R**)-**5g**.

The finding that the *erythro*-configurated hydroperoxides are formed mainly without participation of the HO group seems to be general. Were transition states A (*threo* product) and B (*erythro* product) the only precursors for (*S*,S**)-**2** and (*S*,R**)-**2** (Scheme II), the 1,3-allylic strain[18] should grow with increasing size of the alkyl group R^1 at the chiral hydroxy-bearing carbon. Hence, structure A should become more decisive relative to B and thus an increase in the *threo* diastereoselectivity would have been expected. The experimental results are not in accord with this expectation since the degree of stereodifferentiation for the alcohols **1f,h–j** possessing R^1 groups of different size (Scheme I, R^1 = Me, Et, *i*-Pr, *t*-Bu) is identical within experimental error (entries 8 and 10–12, Table I). Also these findings speak against significant involvement of the hydroxy functionality in the formation of the *erythro* hydroperoxides. More likely, these diastereomers arise from the *classical* singlet oxygen ene reaction (structures C and D, Scheme I) as competing pathway.

(f) *The double bond of the allylic hydroperoxides is formed stereoselectively.* This is demonstrated in the photooxygenation of **1k** (entry 13, Table I). As expected, the hydroperoxy functionality is introduced highly *threo*-selectively. The advantageous feature of this case is that the *E*-configurated hydroperoxides are exclusively formed; none of the corresponding Z-isomers were detected.

Again, the concept of allylic strain[18] offers an explanation for this double stereoselective reaction (Scheme V). The conformer **1k**(Z+), from which the Z-configurated hydroperoxides [*S*,S**-(Z)]- and [*S*,R*-(Z)]-**2k** would arise, is destabilized by severe 1,3-allylic strain[18] due to interactions between the *n*-Pr group and the chiral substituent. On the other hand, such allylic interactions are minimized in the conformer **1k**(E+), which leads to the *E*-configurated hydroperoxides [*S*,S**-(*E*)]- and [*S*,R**-(*E*)]-**2k**. Of the latter, the *E*-*threo*-configurated hydroperoxide [*S*,S**-(*E*)]-**2k** is preferentially formed by the favored HO-assisted pathway (entry 13, Table I).

Conclusions

The ene reaction of $^1O_2$ with chiral allylic alcohols **1** proceeds in high regio- and diastereoselectivity through control by 1,3-allylic strain, provided efficient coordination between $^1O_2$ and the hydroxy group of the substrate operates. Similar directive effects are expected to occur for other nucleophilic functional groups which are capable of interacting with the electrophilic singlet oxygen as enophile. Such control of stereoselectivity should not be limited to the ene reaction, but should also be applicable to [4 + 2] cycloadditions of $^1O_2$. Moreover, by employing enantiomerically pure chiral substrates, a variety of optically

active oxyfunctionalized products would become conveniently available, which should constitute valuable building blocks for asymmetric synthesis.

Experimental Section

General Aspects. IR spectra were recorded with a Perkin-Elmer infrared recording spectrometer 1420 and ^{1}H and ^{13}C NMR spectra with a Bruker AC 200, a Bruker AC 250, or a Bruker WM 400 spectrometer. Elemental analyses were performed in the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Würzburg. For TLC runs Machery und Nagel Polygram SIL G/UV$_{254}$ plates were used; spots were detected with phosphomolybdic acid test spray; for hydroperoxides the KI test was additionally employed. Column-chromatographical purifications were performed on silica gel (63–200 μm) from Woelm, Erlangen. Commercial reagents and solvents were purified according to literature procedures to match reported physical and spectral data. Allylic alcohols and derivatives **1** were prepared according to literature procedures; cf. references given for each particular compound.

CAUTION! Hydroperoxides are potentially dangerous and should be handled with care!

General Procedure for the Photooxygenation of Allylic Alcohols and Derivatives. A solution of the particular substrate (2.0–5.2 mmol) and ca. 2 mg of tetraphenylporphine in 80 mL of CCl_4 was irradiated with two external Philips G/98/2 SON 150-W sodium lamps at 0 °C while a stream of dry oxygen gas was passed continuously through the reaction mixture. The course of the reaction was monitored by means of TLC; after all starting material had been consumed, the solvent was evaporated (20 °C/18 Torr) and the composition of the crude reaction mixture was determined by ^{1}H and ^{13}C NMR (for product ratios cf. Tables I and II, error ±5%). Further purification by column chromatography on silica gel eluting with mixtures of petroleum ether (50–60 °C) (PE) and ether afforded analytically pure samples of the hydroperoxides **2** as colorless oils.

Photooxygenation of 4-Methyl-3-penten-2-ol[20] (**1a**). From 401 mg (4.00 mmol) of **1a** was obtained after 4 h and chromatography (PE:ether, 60:40) 471 mg (89%) of **2a**.

3-Hydroperoxy-4-methyl-4-penten-2-ol [(*S*,S**)-**2a**]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.09 (d, 3 H, J = 6.4 Hz), 1.70 (dd, 3 H, J = 1.3 Hz, J = 1.0 Hz), 3.63 (br s, 1 H), 3.84 (dq, 1 H, J = 8.6 Hz, J = 6.4 Hz), 4.12 (d, 1 H, J = 8.6 Hz), 5.08–5.10 (m, 2 H), 9.44 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 18.4 (q), 19.1 (q), 67.7 (d), 95.3 (d), 117.2 (t), 141.6 (s). (*S*,R**)-**2a**: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.18 (d, 3 H, J = 6.4 Hz), 1.78 (dd, 3 H, J = 1.2 Hz, J = 1.0 Hz), 2.54 (br s, 1 H), 3.95 (dq, 1 H, J = 6.4 Hz, J = 4.9 Hz), 4.28 (d, 1 H, J = 4.9 Hz), 5.04–5.06 (m, 2 H), 9.17 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 18.6 (q), 19.6 (q), 67.4 (d), 92.8 (d), 115.9 (t), 141.6 (s); IR (cm^{-1}) 3700–3040, 1660.

The formation of **2a** in the photooxygenation of **1a** with methanol as solvent has already been described;[21] unfortunately no dr values were reported.

3-Hydroxy-3,5,5-trimethyl-1,2-dioxolane (4a): ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.35 (s, 3 H), 1.38 (s, 3 H), 1.53 (s, 3 H), 2.39 (d, 1 H, J = 12.8 Hz), 2.49 (d, 1 H, J = 12.8 Hz), 3.00 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 23.2 (q), 24.8 (q), 27.3 (q), 58.6 (t), 84.0 (s), 106.1 (s); IR (cm^{-1}) 3640–3280, 1660.

Dioxolane **4a** could not be isolated due to the too low concentration; it was identified in the crude reaction mixture by comparison of the NMR spectral data with those of an authentic sample.[12]

Photooxygenation of 2-Methyl-4-[(trimethylsilyl)oxy]-2-pentene[22] (**1b**). From 900 mg (5.22 mmol) of **1b** was obtained after 8 h and chromatography (PE:ether, 80:20) 672 mg (63%) of **2b**.

2-Methyl-4-[(trimethylsilyl)oxy]-1-penten-3-yl hydroperoxide [(*S*,S**)-**2b**]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.15 (s, 9 H), 1.10 (d, 3 H, J = 6.3 Hz), 1.74 (dd, 3 H, J = 1.3 Hz, J = 1.0 Hz), 3.91 (dq, 1 H, J = 7.7 Hz, J = 6.3 Hz), 4.19 (d, 1 H, J = 7.7 Hz), 4.98–5.05 (m, 2 H), 9.13 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 0.6 (q), 19.2 (q), 20.8 (q), 69.7 (d), 94.1 (d), 116.1 (t), 141.9 (s). (*S*,R**)-**2b**: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.19 (s, 9 H), 1.16 (d, 3 H, J = 6.3 Hz), 1.77 (dd, 3 H, J = 1.1 Hz, 1.0 Hz), 3.95 (dq, 1 H, J = 6.3 Hz, J = 4.6 Hz), 4.27 (d, 1 H, J = 4.6 Hz), 4.98–5.05 (m, 2 H), 8.88 (br s, 1 H); ^{13}C NMR (CDCl$_3$,

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63 MHz) δ 0.4 (q), 19.6 (q), 20.2 (q), 69.4 (d), 92.7 (d), 116.1 (t), 141.9 (s); IR (cm⁻¹) 3650–3250, 1660, 1270. Anal. Calcd for $C_9H_{20}O_3Si$: C, 52.90; H, 9.87. Found: C, 53.21; H, 10.03.

Photooxygenation of 4-[[(Dimethyl(1,1-dimethylethyl)silyl]oxy]-2-methyl-2-pentene[23] (1c). From 994 mg (4.65 mmol) of 1c was obtained after 8 h and chromatography (PE:ether, 80:20) 668 mg (58%) of 2c.

4-[[(Dimethyl(1,1-dimethylethyl)silyl]oxy]-2-methyl-1-penten-3-yl hydroperoxide [(S*,S*)-2c]: ¹H NMR (CDCl₃, 250 MHz) δ 0.11 (s, 3 H), 0.14 (s, 3 H), 0.91 (s, 9 H), 1.10 (d, 3 H, J = 6.3 Hz), 1.75 (dd, 3 H, J = 1.3 Hz, J = 1.0 Hz), 3.95 (dq, 1 H, J = 7.6 Hz, J = 6.3 Hz), 4.21 (d, 1 H, J = 7.6 Hz), 4.98–5.06 (m, 2 H), 8.85 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ –4.3 (q), –4.2 (q), 18.5 (s), 19.4 (q), 20.7 (q), 26.2 (q), 69.8 (d), 94.2 (d), 115.9 (t), 141.9 (s). (S*,R*)-2c: ¹H NMR (CDCl₃, 250 MHz) δ 0.08 (s, 3 H), 0.12 (s, 3 H), 0.88 (s, 9 H), 1.18 (d, 3 H, J = 6.3 Hz), 1.78 (dd, 3 H, J = 1.1 Hz, J = 1.0 Hz), 4.00 (dq, 1 H, J = 6.3 Hz, J = 4.6 Hz), 4.30 (d, 1 H, J = 4.6 Hz), 4.98–5.06 (m, 2 H), 8.78 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ –4.6 (q), –4.2 (q), 18.5 (s), 19.7 (q), 20.1 (q), 26.1 (q), 69.7 (d), 92.7 (d), 115.0 (t), 114.9 (s); IR (cm⁻¹) 3660–3320, 1680, 1270. Anal. Calcd for $C_{12}H_{26}O_3Si$: C, 58.49; H, 10.63. Found: C, 58.76; H, 10.64.

Photooxygenation of 4-Methoxy-2-methyl-2-pentene[24] (1d). From 579 mg (5.07 mmol) of 1d was obtained after 8 h and chromatography (PE: ether, 70:30) 423 mg (57%) of 2d.

4-Methoxy-2-methyl-1-penten-3-yl hydroperoxide [(S*,S*)-2d]: ¹H NMR (CDCl₃, 250 MHz) δ 1.08 (d, 3 H, J = 6.3 Hz), 1.74 (dd, 3 H, J = 1.2 Hz, J = 1.0 Hz), 3.41 (s, 3 H), 3.48 (dq, 1 H, J = 8.3 Hz, J = 6.3 Hz), 4.28 (d, 1 H, J = 8.3 Hz), 5.02–5.06 (m, 2 H), 9.64 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 15.5 (q), 17.9 (q), 59.6 (q), 77.3 (d), 92.9 (d), 116.0 (t), 141.4 (s); IR (cm⁻¹) 3600–3160, 1650. Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.15; H, 9.64. (S*,R*)-2d: ¹H NMR (CDCl₃, 250 MHz) δ 1.16 (d, 3 H, J = 6.4 Hz), 1.74–1.77 (m, 3 H), 3.37 (s, 3 H), 3.49 (dq, 1 H, J = 6.4 Hz, J = 4.5 Hz), 4.39 (d, 1 H, J = 4.5 Hz), 5.02–5.08 (m, 2 H), 9.04 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 14.6 (q), 18.6 (q), 55.7 (q), 76.7 (d), 90.6 (d), 114.5 (t), 141.3 (s); IR (cm⁻¹) 3580–3180, 1645. Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 56.82; H, 10.18.

Photooxygenation of 4-Methyl-3-penten-2-ol Acetate[25] (1e). From 498 mg (3.50 mmol) of 1e was obtained after 8 h a mixture of 2e and 3e. Chromatography (PE:ether, 80:20) gave 668 mg (58%) of 2e, of which 104 mg of (S*,S*)-2e and 176 mg of (S*,R*)-2e were isolated in diastereomerically pure form.

4-Acetoxy-2-methyl-1-penten-3-yl hydroperoxide [(S*,S*)-2e]: ¹H NMR (CDCl₃, 400 MHz) δ 1.21 (d, 3 H, J = 6.5 Hz), 1.82 (dd, 3 H, J = 1.5 Hz, J = 0.9 Hz), 2.10 (s, 3 H), 4.20 (d, 1 H, J = 8.1 Hz), 5.07–5.14 (m, 2 H), 5.15 (dq, 1 H, J = 8.1 Hz, J = 6.5 Hz), 9.44 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 16.5 (q), 18.1 (q), 20.7 (q), 68.8 (d), 90.7 (d), 116.3 (t), 140.8 (s); IR (cm⁻¹) 3620–3260, 1740, 1650. Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.54; H, 8.23. (S*,R*)-2e: ¹H NMR (CDCl₃, 400 MHz) δ 1.23 (d, 3 H, J = 6.6 Hz), 1.77 (t, 3 H, J = 1.3 Hz), 2.11 (s, 3 H), 4.34 (dd, 1 H, J = 3.7 Hz, J = 0.5 Hz), 5.00–5.02 (m, 1 H), 5.10–5.12 (m, 1 H), 5.38 (dq, 1 H, J = 6.6 Hz, J = 3.7 Hz), 9.44 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 15.5 (q), 18.8 (q), 20.9 (q), 68.5 (d), 89.9 (d), 116.1 (t), 140.0 (s), 171.5 (s); IR (cm⁻¹) 3600–3400, 1720, 1640. Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.47; H, 8.30.

(E)-4-Hydroperoxy-4-methyl-2-penten-2-ol acetate[(E)-3e]: ¹H NMR (CDCl₃, 400 MHz) δ 1.42 (s, 6 H), 2.04 (d, 3 H, J = 1.1 Hz), 2.13 (s, 3 H), 5.20 (d, 1 H, J = 1.1 Hz), 9.44 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 20.2 (q), 22.2 (q), 25.7 (q), 80.2 (s), 121.9 (d), 148.2 (s), 170.2 (s).

(Z)-4-Hydroperoxy-4-methyl-2-penten-2-ol acetate [(Z)-3e]: ¹H NMR (CDCl₃, 400 MHz) δ 1.36 (s, 6 H), 1.90 (d, 3 H, J = 1.1 Hz), 2.31 (s, 3 H), 5.11 (d, 1 H, J = 1.1 Hz), 9.44 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 20.0 (q), 20.7 (q), 25.1 (q), 80.7 (s), 120.3 (d), 146.8 (s), 171.2 (s).

The labile enol acetates 3e could not be isolated and purified by chromatographic methods, so that the NMR data were extracted from the crude reaction mixture by comparison with those of the isolated and fully characterized hydroperoxides 2e.

Photooxygenation of (Z)-3-Penten-2-ol[26] (1f). From 440 mg (5.11 mmol) of 1f was obtained after 6 h and chromatography (PE:ether, 80:20) 443 mg (73%) of (Z)-2f.

3-Hydroperoxy-4-penten-2-ol [(S*,S*)-1f]: ¹H NMR (CDCl₃, 250 MHz) δ 1.16 (d, 3 H, J = 6.4 Hz), 2.92 (br s, 1 H), 3.86 (dq, 1 H, J = 7.9 Hz, J = 6.4 Hz), 4.19 (dd, 1 H, J = 7.9 Hz, J = 7.8 Hz), 5.38 (dd, 1 H, J = 10.3 Hz, J = 1.6 Hz), 5.42 (dd, 1 H, J = 17.4 Hz, J = 1.6 Hz), 5.78 (ddd, 1 H, J = 17.4 Hz, J = 10.3 Hz, J = 7.8 Hz), 9.00 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 18.7 (q), 68.0 (d), 91.6 (d), 120.9 (t), 133.5 (d). (S*,R*)-1f: ¹H NMR (CDCl₃, 250 MHz) δ 4.20 (dd, 1 H, J = 6.6 Hz, J = 2.9 Hz), 4.30 (dd, 1 H, J = 7.7 Hz, J = 2.9 Hz), the signals are partially overlapped by those of the S*,S* diastereomer, and therefore, only the separated resonances are given; ¹³C NMR (CDCl₃, 63 MHz) δ 20.7 (q), 67.1 (d), 90.0 (d), 121.6 (t), 131.5 (d); IR (cm⁻¹) 3600–3040, 1635. Anal. Calcd for $C_5H_{10}O_3$: C, 50.84; H, 8.53. Found: C, 50.43; H, 8.80.

Photooxygenation of (E)-3-Penten-2-ol[27][(E)-1f)]. Photooxygenation (20 h) of a solution of 105 mg (1.22 mmol) of (E)-1f in 20 mL of CCl₄ gave in addition to 2f also 4% of 4f (1:1 mixture of both diastereomers).

3-Hydroxy-3,5-dimethyl-1,2-dioxolane (4f): ¹H NMR (CDCl₃, 250 MHz) δ 2.15 (dd, 1 H, J = 12.6 Hz, J = 7.5 Hz), 2.25 (dd, 1 H, J = 12.7 Hz, J = 8.3 Hz), 2.71 (dd, 1 H, J = 12.7 Hz, J = 7.5 Hz), 2.84 (dd, 1 H, J = 12.6 Hz, J = 7.0 Hz), the signals are partially overlapped by those of other compounds, and therefore, only the separated resonances ae given; ¹³C NMR (CDCl₃, 63 MHz) δ 20.4 (q), 20.9 (q), 22.9 (q), 23.4 (q), 53.7 (t), 53.9 (t), 77.2 (d), 78.5 (d), 105.1 (s), 106.3 (s).

The dioxolanes 4f could not be isolated due to too low concentration. The NMR data were extracted with the crude reaction mixture by comparison with those of the isolated and fully characterized hydroperoxides 2f. Moreover, the spectral characteristics were similar to those observed for dioxolane 4a.

Photooxygenation of 3-Methyl-3-penten-2-ol[15d] (1g). The conversion (5 h) of 501 mg (5.00 mmol) of 1g (Z:E = 85:15) afforded a mixture of 87% of 2g [(S*,S*):(S*,R*) = 88:12] and 13% of 5g [(S*,S*):(S*,R*) = 31:69]. By chromatographic purification (PE:ether, 80:20) 380 mg (58%) of 2g and 60 mg (9%) of 5g were isolated. The photooxygenation (5 h) of 200 mg (2.00 mmol) of (Z)-1g in 40 mL of CCl₄ gave the crude product, which consisted of 92% of 2g [(S*,S*):(S*,R*) = 93:7] and 8% of 5g [(S*,S*):(S*,R*) = 23:77]. When the reaction was repeated with 202 mg (2.02 mmol) of 1g (Z:E = 36:64), a mixture of 68% of 2g [(S*,S*): (S*,R*) = 76:24] and 32% of 5g [(S*,S*):(S*,R*) = 49:51] was obtained. From these product ratios the product distribution for the conversion of (E)-1g was extrapolated.

3-Hydroperoxy-3-methyl-4-penten-2-ol [(S*,S*)-2g]: ¹H NMR (CDCl₃, 40 MHz) δ 1.14 (d, 3 H, J = 6.5 Hz), 1.28 (s, 3 H), 2.55 (br s, 1 H), 4.02 (q, 1 H, J = 6.5 Hz), 5.35 (dd, 1 H, J = 11.0 Hz, J = 1.1 Hz), 5.38 (dd, 1 H, J = 17.7 Hz, J = 1.1 Hz), 5.92 (dd, 1 H, J = 17.7 Hz, J = 11.0 Hz), 8.15 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 15.0 (q), 17.3 (q), 70.1 (d), 87.4 (s), 117.6 (t), 138.2 (d). (S*,R*)-2g: ¹H NMR (CDCl₃, 400 MHz) δ 1.14 (d, 3 H, J = 6.6 Hz), 1.34 (s, 3 H), 2.55 (br s, 1 H), 4.01 (q, 1 H, J = 6.6 Hz), 5.36 (dd, 1 H, J = 17.7 Hz, J = 1.1 Hz), 5.39 (dd, 1 H, J = 11.2 Hz, J = 1.1 Hz), 5.99 (dd, 1 H, J = 17.7 Hz, J = 11.2 Hz), 8.15 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 18.5 (q), 71.1 (d), 87.4 (s), 118.7 (t), 135.9 (d); IR (cm⁻¹) 3700–3050, 1650. Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.58; H, 9.24.

4-Hydroperoxy-3-methylenepentan-2-ol [(S*,S*)-5g]: ¹H NMR (CDCl₃, 400 MHz) δ 1.39 (d, 3 H, J = 6.6 Hz), 1.40 (d, 3 H, J = 6.5 Hz), 2.83 (br s, 1 H), 4.44 (dq, 1 H, J = 6.5 Hz, J = 0.9 Hz), 4.64 (dq, 1 H, J = 6.6 Hz, J = 0.8 Hz), 5.22 (m, 1 H), 5.32 (m, 1 H), 9.18 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 19.1 (q), 22.4 (q), 69.3 (d), 81.8 (d), 112.8 (t), 152.1 (s). (S*,R*)-5g: ¹H NMR (CDCl₃, 400 MHz) δ 1.30 (d, 3 H, J = 6.6 Hz), 1.40 (d, 3 H, J = 6.5 Hz), 2.83 (br s, 1 H), 4.50 (dq, 1 H, J = 6.5 Hz, J = 0.7 Hz), 4.72 (q, 1 H, J = 6.6 Hz), 5.22 (m, 1 H), 5.32 (m, 1 H), 9.18 (br s, 1 H); ¹³C NMR (CDCl₃, 63 MHz) δ 18.4 (q), 22.1 (q), 67.1 (d), 82.6 (d), 114.5 (t), 151.4 (s); IR (cm⁻¹) 3700–3080, 1630. Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 53.95; H, 9.43.

Photooxygenation of (Z)-4-Hexen-3-ol[28] [(Z)-1h]. From 346 mg (3.45 mmol) of Z-1h was obtained after 5.5 h and chromatography (PE: ether, 50:50) 392 mg (85%) of 2h.

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4-Hydroperoxy-5-hexen-3-ol [(S*,S*)-2h]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.96 (t, 3 H, $J = 7.4$ Hz), 1.28–1.64 (m, 2 H), 2.80 (br s, 1 H), 3.61 (dt, 1 H, $J = 7.9$ Hz, $J = 3.5$ Hz), 4.21 (dd, 1 H, $J = 7.9$ Hz, $J = 7.8$ Hz), 5.38 (dd, 1 H, $J = 10.3$ Hz, $J = 1.6$ Hz), 5.42 (dd, 1 H, $J = 17.4$ Hz, $J = 1.6$ Hz), 5.81 (ddd, 1 H, $J = 17.4$ Hz, $J = 10.3$ Hz, $J = 7.8$ Hz), 8.97 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 9.5 (q), 25.5 (t), 73.1 (d), 90.2 (d), 120.8 (t), 133.5 (d). **(S*,R*)-2h:** ^{1}H NMR (CDCl$_3$, 250 MHz) δ 3.93 (dt, 1 H, $J = 6.8$ Hz, $J = 2.8$ Hz), 4.36 (dd, 1 H, $J = 7.8$ Hz, $J = 2.8$ Hz), the signals are partially overlapped by those of the S*,S* diastereomer, and only the separated resonances are given; ^{13}C NMR (CDCl$_3$, 63 MHz) δ 10.2 (q), 25.1 (t), 72.5 (d), 89.2 (d), 121.6 (t), 131.4 (d); IR (cm^{-1}) 3600–3040, 1635. Anal. Calcd for C$_6$H$_{12}$O$_3$: C, 54.53; H, 9.15. Found: C, 54.42; H, 9.51.

Photooxygenation of (Z)-2-Methyl-4-hexen-3-ol[29][(Z)-1i]). From 245 mg (1.74 mmol) of (Z)-1i (40 mL of CCl$_4$) was obtained after 5.5 h and chromatography (PE:ether, 50:50) 202 mg (79%) of 2i.

4-Hydroperoxy-2-methyl-5-hexen-3-ol[(S*,S*)-2i]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.89 (d, 3 H, $J = 6.8$ Hz), 1.00 (d, 3 H, $J = 6.9$ Hz), 1.70–1.86 (m, 1 H), 2.44 (br s, 1 H), 3.48 (dd, 1 H, $J = 7.8$ Hz, $J = 3.5$ Hz), 4.32 (dd, 1 H, $J = 7.9$ Hz, $J = 7.8$ Hz), 5.39 (d, 1 H, $J = 10.2$ Hz), 5.47 (d, 1 H, $J = 17.3$ Hz), 5.82 (ddd, 1 H, $J = 17.3$ Hz, $J = 10.2$ Hz, $J = 7.9$ Hz), 8.76 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 15.0 (q), 19.9 (q), 29.2 (d), 76.0 (d), 88.5 (d), 120.5 (t), 133.6 (d). **(S*,R*)-2i:** ^{1}H NMR (CDCl$_3$, 250 MHz) δ 3.65 (dd, 1 H, $J = 8.3$ Hz, $J = 3.1$ Hz), 4.66 (dd, 1 H, $J = 7.9$ Hz, $J = 3.1$ Hz), the signals are partially overlapped by those of the S*,S* diastereomer, and only the separated resonances are given; ^{13}C NMR (CDCl$_3$, 63 MHz) δ 14.8 (q), 18.6 (q), 30.0 (d), 75.6 (d), 87.6 (d), 121.7 (t), 131.1 (d); IR (cm^{-1}) 3660–3060, 1640. Anal. Calcd for C$_7$H$_{14}$O$_3$: C, 57.51; H, 9.65. Found: C, 57.86; H, 9.87.

Photooxygenation of (Z)-2,2-Dimethyl-4-hexen-3-ol[30][(Z)-1j]). After photooxygenation of a solution of 200 mg (1.56 mmol) of 1j and 35 mg (0.16 mmol) of 2,6-di-*tert*-butyl-4-methylphenol in 40 mL of CCl$_4$ for 7 h, 200 mg (80%) of 2j was isolated on chromatography (PE:ether, 80:20). In the absence of 2,6-di-*tert*-butyl-4-methylphenol, 2j is unstable under photooxygenation conditions; in this case 2j is converted to 6j.

2,2-Dimethyl-4-hydroperoxy-5-hexen-3-ol [(S*,S*)-2j]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.00 (s, 9 H), 2.46 (br s, 1 H), 3.37 (d, 1 H, $J = 5.2$ Hz), 4.43 (dd, 1 H, $J = 7.8$ Hz, $J = 5.2$ Hz), 5.40 (dd, 1 H, $J = 10.3$, $J = 0.9$ Hz), 5.43 (dd, 1 H, $J = 17.4$ Hz, $J = 0.9$ Hz), 6.03 (ddd, 1 H, $J = 17.4$ Hz, $J = 10.3$ Hz, $J = 7.8$ Hz), 9.14 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 26.6 (q), 34.7 (s), 80.2 (d), 86.8 (d), 119.9 (t), 135.6 (d). **(S*,R*)-2j:** ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.97 (s, 9 H), 3.55 (d, 1 H, $J = 2.5$ Hz), 4.48 (dd, 1 H, $J = 8.2$ Hz, $J = 2.5$ Hz), the signals are partially overlapped by those of the S*,S* diastereomer, and only the separated resonances are given; ^{13}C NMR (CDCl$_3$, 63 MHz) δ 26.4 (q), 34.1 (s), 77.2 (d), 87.8 (d), 122.2 (t), 132.4 (d); IR (cm^{-1}) 3680–3160, 1640. Anal. Calcd for C$_8$H$_{16}$O$_3$: C, 59.98; H, 10.07. Found: C, 59.91; H, 10.08.

(E)-2,2-Dimethyl-6-hydroperoxy-4-hexen-3-ol (6j): ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.90 (s, 9 H), 2.46 (br s, 1 H), 3.82 (d, 1 H, $J = 5.5$ Hz), 4.51 (d, 2 H, $J = 5.3$ Hz), 5.77–5.96 (m, 2 H), 9.26 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 25.5 (q), 34.7 (s), 76.9 (t), 80.1 (d), 126.6 (d), 135.9 (d); IR (cm^{-1}) 3680–3120, 1640. Anal. Calcd for C$_8$H$_{16}$O$_3$: C, 59.98; H, 10.07. Found: C, 60.34; H, 9.73.

Photooxygenation of (Z)-3-Octen-2-ol[31][(Z)-1k]). From 256 mg (2.00 mmol) of (Z)-1k was obtained after 4 h and chromatography (PE:ether, 50:50) 224 mg (70%) of 2k.

3-Hydroperoxy-4-octen-2-ol[[S*,S*-(E)]-2k]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.91 (t, 3 H, $J = 7.3$ Hz), 1.16 (d, 1 H, $J = 6.4$ Hz), 1.44 (tq, 2 H, $J = 7.5$ Hz, $J = 7.3$ Hz), 2.02–2.15 (m, 2 H), 2.90 (br s, 1 H), 3.87 (dq, 1 H, $J = 8.2$ Hz, $J = 6.4$ Hz), 4.12 (dd, 1 H, $J = 8.4$ Hz, $J = 8.2$ Hz), 5.39 (ddt, 1 H, $J = 15.5$ Hz, $J = 8.4$ Hz, $J = 1.5$ Hz), 5.84 (dt, 1 H, $J = 15.5$ Hz, $J = 6.7$ Hz), 8.83 (br s, 1 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 13.8 (q), 19.1 (q), 25.2 (t), 34.7 (t), 68.7 (d), 91.7 (d), 125.3 (d), 138.5 (d). **[S*,R*-(E)]-2k:** ^{1}H NMR (CDCl$_3$, 250 MHz) δ 4.18 (dq, 1 H, $J = 6.6$ Hz, $J = 3.0$ Hz), 4.27 (dd, 1 H, $J = 8.3$ Hz, $J = 3.0$ Hz), 5.49 (ddt, 1 H, $J = 15.5$ Hz, $J = 8.3$ Hz, $J = 1.5$ Hz), the signals are partially overlapped by those of the S*,S* diastereomer, and only the separated resonances are given; ^{13}C NMR (CDCl$_3$, 63 MHz) δ 13.8 (q), 17.9 (q), 22.2 (t), 34.9 (t), 67.3 (d), 90.1 (d), 122.7 (t), 139.6 (d); IR

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(cm^{-1}) 3660–3080, 1665. Anal. Calcd for C$_8$H$_{16}$O$_3$: C, 59.98; H, 10.07. Found: C, 60.23; H, 10.40.

General Procedure for the Catalytic Hydrogenation of Allylic Hydroperoxides. A solution of the allylic hydroperoxide (0.45–1.6 mmol) in methanol (5–15 mL) was hydrogenated at room temperature and normal pressure of hydrogen gas with ca. 5 mg of PtO$_2$. The catalyst was removed by filtration and the solvent rotoevaporated (20 °C/18 Torr). In each case the dr values of the saturated diol and the corresponding allylic hydroperoxide were identical.

Hydrogenation of 3-Hydroperoxy-4-methyl-4-penten-2-ol (2a). From 215 mg (1.63 mmol) of 2a [(S*,S*):(S*,R*) = 93:7] in 15 mL of methanol was isolated after 2 h 179 mg (93%) of 7a as colorless prisms, mp 49–52 °C (methanol).

4-Methylpentane-2,3-diol[(S*,S*)-7a]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.82 (d, 3 H, $J = 6.8$ Hz), 0.91 (d, 3 H, $J = 6.8$ Hz), 1.12 (d, 3 H, $J = 6.4$ Hz), 1.70 (dsept, 1 H, $J = 6.8$ Hz, $J = 4.7$ Hz), 3.02 (dd, 1 H, $J = 6.2$ Hz, $J = 4.7$ Hz), 3.41 (br s, 2 H), 3.69 (dq, 1 H, $J = 6.4$ Hz, $J = 6.2$ Hz); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 16.5 (q), 20.0 (q), 20.4 (q), 30.2 (d), 68.9 (d), 80.9 (d). **(S*,R*)-7a:** ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.79 (d, 3 H, $J = 6.8$ Hz), 0.94 (d, 3 H, $J = 6.7$ Hz), 1.07 (d, 3 H, $J = 6.4$ Hz), 1.53 (dqq, 1 H, $J = 8.4$ Hz, $J = 6.8$ Hz, $J = 6.7$ Hz), 3.20 (dd, 1 H, $J = 8.4$ Hz, $J = 3.4$ Hz), 3.41 (br s, 2 H), 3.81 (dq, 1 H, $J = 6.4$ Hz, $J = 3.4$ Hz); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 16.1 (q), 19.1 (q), 19.7 (q), 30.7 (d), 68.7 (d), 80.4 (d); IR (cm^{-1}) 3660–3140. The spectral data matched those reported in refs 14b,c,e,g.

Hydrogenation of 3-Hydroperoxy-4-penten-2-ol (2f). Conversion of 105 mg (0.889 mmol) of 2f [(S*,S*):(S*,R*) = 93:7] in 15 mL of methanol gave after 2 h 88 mg (95%) of 7f as a colorless oil.

Pentane-2,3-diol [(S*,S*)-7f]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.99 (t, 3 H, $J = 7.4$ Hz), 1.18 (d, 3 H, $J = 6.3$ Hz), 1.31–1.65 (m, 2 H), 2.70 (br s, 2 H), 3.26 (ddd, 1 H, $J = 8.4$ Hz, $J = 6.4$ Hz, $J = 3.8$ Hz), 3.60 (dq, 1 H, $J = 6.4$ Hz, $J = 6.3$ Hz); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 9.9 (q), 19.4 (q), 26.0 (t), 70.5 (d), 77.5 (d). **(S*,R*)-7f:** ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.14 (d, 3 H, $J = 6.5$ Hz), 3.80 (dq, 1 H, $J = 6.5$ Hz, $J = 3.2$ Hz), the signals are partially overlapped by those of the S*,S* diastereomer, and only the separated resonances are given; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 10.4 (q), 18.3 (q), 24.7 (t), 70.1 (d), 76.4 (d); IR (cm^{-1}) 3650–3040.

The spectral data matched those reported in ref 14j.

Hydrogenation of 3-Hydroperoxy-3-methyl-4-penten-2-ol (2g). From 167 mg (1.26 mmol) of 2g [(S*,S*):(S*,R*) = 76:24] in 15 mL of methanol was obtained after 70 min 140 mg (94%) of 7g as a colorless oil.

3-Methylpentane-2,3-diol [(S*,R*)-7g]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.89 (t, 3 H, $J = 7.5$ Hz), 1.03 (s, 3 H), 1.09 (d, 3 H, $J = 6.5$ Hz), 1.28–1.64 (m, 2 H), 2.74 (br s, 2 H), 3.61 (q, 1 H, $J = 6.5$ Hz); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 7.8 (q), 17.6 (q), 20.1 (q), 31.7 (t), 72.8 (d), 75.4 (s). **(S*,R*)-7f:** ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.11 (d, 3 H, $J = 6.4$ Hz), 3.59 (q, 1 H, $J = 6.4$ Hz), the signals are partially overlapped by those of the S*,S* diastereomer, and only the separated resonances are given; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 7.8 (q), 17.5 (q), 22.9 (q), 28.4 (t), 74.1 (d), 75.1 (s); IR (cm^{-1}) 3640–3080.

The spectral data matched those reported in ref 14f.

Hydrogenation of 4-Hydroperoxy-5-hexen-3-ol (2h). From 112 mg (0.874 mmol) of 2h [(S*,S*):(S*,R*) = 94:6] in 10 mL of methanol was obtained after 2 h 94 mg (94%) of 7h as a colorless oil.

Hexane-3,4-diol [(S*,S*)-7h]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.95 (t, 6 H, $J = 7.4$ Hz), 1.33–1.64 (m, 4 H), 2.28 (br s, 2 H), 3.29–3.36 (m, 2 H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 10.0 (q), 26.3 (t), 75.4 (d). **(S*,R*)-7h:** ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.96 (t, 6 H, $J = 7.4$ Hz), 3.50–3.56 (m, 2 H), the signals are partially overlapped by those of the S*,S* diastereomer, and only the separated resonances are given; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 10.4 (q), 24.0 (t), 76.0 (d); IR (cm^{-1}) 3700–3060.

The spectral data matched those reported in ref 14g.

Hydrogenation of 3-Hydroperoxy-4-octen-2-ol (2k). The conversion of 72 mg (0.449 mmol) of 2k [[S*,S*-(E)]:[S*,R*-(E)] = 94:6] in 5 mL of methanol gave after 1 h 63 mg (96%) of 7k as a colorless oil.

Octane-2,3-diol [(S*,S*)-7k]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.88 (t, 3 H, $J = 6.5$ Hz), 1.17 (d, 3 H, $J = 6.3$ Hz), 1.20–1.52 (m, 8 H), 2.93 (br s, 2 H), 3.31 (dt, 1 H, $J = 6.5$ Hz, $J = 6.3$ Hz), 3.57 (quin, 1 H, $J = 6.3$ Hz); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 14.0 (q), 19.4 (q), 22.5 (t), 25.2 (t), 31.8 (t), 33.3 (t), 70.9 (d), 76.2 (d). **(S*,R*)-7f:** ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.13 (d, 3 H, $J = 6.4$ Hz), 3.77 (dq, 1 H, $J = 6.4$ Hz, $J = 3.2$ Hz), the signals are partially overlapped by those of the S*,S* diastereomer, and only the separated resonances are given; ^{13}C

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NMR (CDCl$_3$, 50 MHz) δ 13.8 (q), 19.8 (q), 23.2 (t), 25.4 (t), 31.5 (t), 32.7 (t), 70.4 (d), 74.9 (d); IR (cm^{-1}) 3680–3220.

The spectral data matched those reported in refs 14b,h,i.

Hydrogenation of 4-Hydroperoxy-3-methylenepentan-2-ol (5g). From 60 mg (0.454 mmol) of 5g [(S^*,S^*):(S^*,R^*) = 68:32] in 5 mL of methanol was obtained after 1 h 49 mg (91%) of 8g [(S^*,R^*,R^*):(S^*,S^*,R^*): (S^*,S^*) = 49:20:31] as a colorless oil.

3-Methylpentane-2,4-diol [(S^*,R^*,R^*)-8g]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.91 (d, 3 H, J = 6.1 Hz), 4.08 (dq, 2 H, J = 6.4 Hz, J = 2.2 Hz). (S^*,S^*,R^*)-8g: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.76 (d, 3 H, J = 6.9 Hz), 3.73 (dq, 2 H, J = 8.5 Hz, J = 6.2 Hz). (S^*,S^*)-8g: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 0.85 (d, 3 H, J = 6.1 Hz), 3.85 (dq, 1 H, J = 6.8 Hz, J = 6.3 Hz), 4.12 (dq, 1 H, J = 6.4 Hz, J = 3.1 Hz). The other observed resonances listed below could not unequivocally be assigned to one of the diastereomers: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.14 (d, 3 H, J = 6.3 Hz), 1.17 (d, 3 H, J = 6.4 Hz), 1.19 (d, 3 H, J = 6.2 Hz), 1.21 (d, 3 H, J = 6.3 Hz), 1.28–1.48 (m, 3 H), 3.12 (br s, 6 H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 4.0 (q), 12.5 (q), 13.4 (q), 19.1 (q), 21.6 (q), 22.2 (q), 22.3 (q), 43.6 (d), 44.6 (d), 47.3 (d), 70.0 (d), 71.1 (d), 72.9 (d), 73.5 (d); IR (cm^{-1}) 3640–3080.

The spectral data matched those reported in refs 14a,d.

Desilylation of 2b. To a solution of 261 mg (1.28 mmol) of 2b [(S^*,S^*): (S^*,R^*) = 80:20] in 5 mL of methanol was added 250 mg of silica gel, and the mixture was stirred at room temperature. After 9 h the silica gel was removed by filtration and the solvent removed (20 °C/18 Torr) to afford 160 mg (95%) of 2a [(S^*,S^*):(S^*,R^*) = 80:20] as a colorless oil. This material was identical with that obtained by photooxygenation of 1a.

Ph$_3$P Reduction of 2a. To a solution of 237 mg (1.79 mmol) of 2a [(S^*,S^*):(S^*,R^*) = 93:7] in 5 mL of CH$_2$Cl$_2$ was added while stirring at 0 °C a solution of 510 mg (1.94 mmol) of Ph$_3$P in 5 mL of CH$_2$Cl$_2$. The reaction mixture was warmed up to room temperature, stirring was continued for 30 min, and the solvent was rotoevaporated (20 °C/18 Torr). Purification of the residue by Kugelrohr distillation at 140 °C (18 Torr) yielded 168 mg (81%) of 9a [(S^*,S^*):(S^*,R^*) = 93:7] as a colorless oil.

4-Methyl-4-penten-2,3-ol [(S^*,S^*)-9a]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.08 (d, 3 H, J = 6.5 Hz), 1.68 (d, 3 H, J = 0.6 Hz), 3.13 (br s, 2 H), 3.67–3.78 (m, 2 H), 4.86–4.88 (m, 1 H), 4.95 (d, 1 H, J = 0.7 Hz); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 17.7 (q), 18.9 (q), 68.6 (d), 80.6 (d), 113.7 (t), 144.5 (s). (S^*,R^*)-9a: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.07 (d, 3 H, J = 6.3 Hz), 1.71 (s, 3 H), 3.13 (br s, 2 H), 3.85 (dq, 1 H, J = 6.3 Hz, J = 4.5 Hz), 4.01 (d, 1 H, J = 4.5 Hz), 4.90 (s, 1 H), 4.99 (s, 1 H);

^{13}C NMR (CDCl$_3$, 63 MHz) δ 18.6 (q), 19.6 (q), 67.4 (d), 92.8 (d), 115.9 (t), 141.6 (s); IR (cm^{-1}) 3640–3000, 1650.

The spectral data matched those reported in ref 32.

LiAlH$_4$ Reduction of (S^*,R^*)-3e. To a suspension of 191 mg (5.02 mmol) of LiAlH$_4$ in 5 mL of dry ether was added a solution of 350 mg (2.01 mmol) of (S^*,R^*)-3e in 5 mL of ether. After 30 min were added in succession 0.2 mL of water, 0.2 mL of 15% aqueous NaOH, and 0.6 mL of water by means of a syringe (**CAUTION!** Vigorous evolution of hydrogen gas!). The precipitate was removed by filtration, the solvent rotoevaporated (20 °C/18 Torr), and the residue recrystallized from ether to afford 164 mg (70%) of (S^*,R^*)-9a as colorless needles, mp 47 °C (ref 33, 48–49 °C). The spectral data were identical with those above.

m-CPBA Epoxidation of (Z)-1g.^{11} To a solution of 100 mg (1.00 mmol) of (Z)-1g in 20 mL of CH$_2$Cl$_2$ was added at 0 °C portionwise 207 mg (1.20 mmol) of m-CPBA. After 3 h, the solid matter was removed by filtration and the solvent removed (20 °C/18 Torr). The resulting colorless oil contained *threo-* and *erythro-*10 in a 90:10 ratio.

3,4-Epoxy-3-methylpentan-2-ol [(S^*,R^*,S^*)-10 (threo-10)]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.20 (d, 3 H, J = 6.7 Hz), 1.29 (s, 3 H), 1.30 (d, 3 H, J = 5.7 Hz), 2.02 (br s, 1 H), 2.96 (q, 1 H, J = 5.7 Hz), 3.69 (q, 1 H, J = 6.7 Hz); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 13.7 (q), 15.8 (q), 19.0 (q), 60.8 (d), 64.4 (s), 69.0 (d). [(S^*,S^*,R^*)-10 (erythro-10)]: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.27 (s, 3 H), 1.27 (d, 3 H, J = 6.3 Hz), 1.42 (d, 3 H, J = 5.8 Hz), 1.83 (br s, 1 H), 2.95 (q, 1 H, J = 5.8 Hz), 3.77 (q, 1 H, J = 6.3 Hz); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 13.5 (q), 17.7 (q), 18.6 (q), 61.3 (d), 62.8 (s), 67.8 (d); IR (cm^{-1}) 3640–3240.

VO(acac)$_2$/t-BuOOH Epoxidation of (Z)-1g^{11}: A mixture of 0.48 mL of 3.1 M t-BuOOH (1.50 mmol) in CH$_2$Cl$_2$, 100 mg (1.00 mmol) of (Z)-1g, and 2.7 mg (1 mol %) of VO(acac)$_2$ in 20 mL of CH$_2$Cl$_2$ was stirred at 0 °C for 12 h. The solution was washed with 1 mL of saturated, aqueous Na$_2$SO$_3$ solution and water (2 × 2 mL) and dried over MgSO$_4$ and the solvent rotoevaporated (20 °C/18 Torr). The residual oil consisted of *threo-* and *erythro-*10 in a 33:67 ratio. The spectral data were identical with those above.

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