A Highly Diastereoselective Dioxetane Formation by the Hydroxy-Directed [2+2] Cycloaddition of Singlet Oxygen to a Chiral Allylic Alcohol

Waldemar Adam,* Chantu R. Saha-Möller, and Simon B. Schambony

Contribution from the Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

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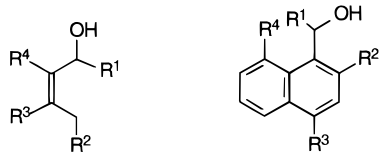
Abstract: The adamantylidene-substituted allylic alcohol **1a** reacts diastereoselectively with singlet oxygen in $CDCl_3$ to yield the dioxetane *threo*-**2a**, accompanied by the dioxolane **4**, which is formed as a subsequent product of an initial ene reaction. In the more polar CD_3OD/CCl_4 solvent mixture, the diastereoselectivity drops to 89:11, but the ene mode (dioxolane **4**) is completely suppressed. In contrast, the photooxygenation of the acetate **1b** in $CDCl_3$ and in CD_3OD yielded only ene product **3b**. The observed *threo*-selective hydroxy-group directivity is explained in terms of hydrogen bonding in the exciplex between the singlet oxygen and the hydroxy group, and the latter is appropriately conformationally aligned in the substrate by 1,3-allylic strain. This synergism between conformational strain and hydrogen bonding controls not only the stereochemical course but also the mode selectivity (ene, [4+2], and [2+2]) in all three reaction types of singlet oxygen.

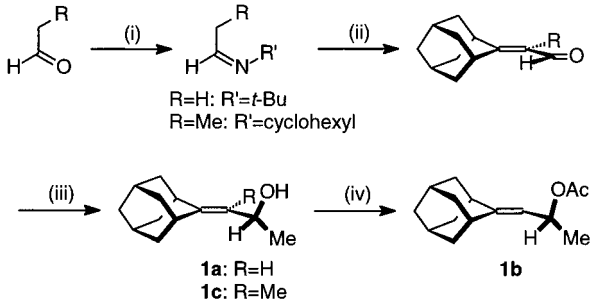
Introduction

The directing property of the hydroxy functionality is well-known for the ene[1] and [4+2] cycloaddition[2] modes of singlet oxygen ($^1O_2$). It has been observed in the photooxygenation of chiral allylic (Structure **A**) or naphthylic (Structure **B**) alcohols,



in which the π-facial selectivity derives from the conformational fixation of the chiral center, which places the hydroxy group into a favorable geometrical arrangement for hydrogen bonding with the attacking singlet oxygen. The present study addresses the question, whether this hydroxy-group directivity also applies in the [2+2] cycloaddition of singlet oxygen to chiral allylic alcohols with allylic strain. Moreover, capping of the allylic hydroxy functionality by means of acylation should annihilate the hydroxy-group directivity and enhance, therewith, the ene reactivity. For this purpose, the chiral adamantylidene-substituted allylic alcohols **1** were chosen as substrates: On one hand, the adamantane ring bears no abstractable allylic hydrogen atoms and is, therefore, not prone to ene reaction, except for the allylic hydrogen atom at the chirality center; on the other hand, spiroadamantane substitution stabilizes the resulting 1,2-dioxetanes and makes these thermally labile peroxides easier to handle.[3] Herein we report novel results, which demonstrate that, indeed, the hydroxy group directs *threo*-diastereoselectively also the [2+2] cycloaddition mode of $^1O_2$, but acetylation promotes mode-selectively ene reaction.

Scheme 1



(i) $R'NH_2$, KOH; (ii) 1. LDA, THF, 2. $(EtO)_2POCl$, THF, 3. adamantanone, THF, 4. H_3O^+; (iii) MeLi, THF/Et_2O; (iv) Ac_2O, pyridine.

Results and Discussion

The chiral allylic substrates **1** were synthesized by a modified aldol condensation, followed by reaction with methyllithium (Scheme 1). The allylic alcohol **1a** and the acetate **1b** were photooxygenated at low temperature (−10 °C or below) in $CDCl_3$ or CD_3OD by using 5,10,15,20-tetrakis(pentafluorophenyl)porphine (TPFPP) or methylene blue as sensitizers (Scheme 2). The photooxygenation of alcohol **1a** in $CDCl_3$ yielded only one of the two possible diastereomeric dioxetanes **2a** through the [2+2] cycloaddition, as well as the hydroperoxide **3a** by the ene reaction of singlet oxygen, but the latter was observed in the form of its cyclic tautomer, the hydroxydioxolane **4** (Table 1, entry 1). Thus, the [2+2] versus ene mode

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(2) (a) Adam, W.; Prein, M. *J. Am. Chem. Soc.* **1993**, *115*, 3766−2767. (b) Adam, W.; Peters, E. M.; Peters, K.; Prein M.; von Schnering, H. G. *J. Am. Chem. Soc.* **1995**, *117*, 6686−6690. (c) Adam, W.; Prein, M. *Acc. Chem. Res.* **1996**, *29*, 275−283.

(3) (a) Adam, W.; Arias Encarnación, L. A.; Zinner, K. *Chem. Ber.* **1983**, *116*, 839−846. (b) Matsumoto, M.; Watanabe, N.; Kasuga, N. C.; Hamada, F.; Tadokoro, K. *Tetrahedron Lett.* **1997**, *38*, 2863−2866.

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Scheme 2

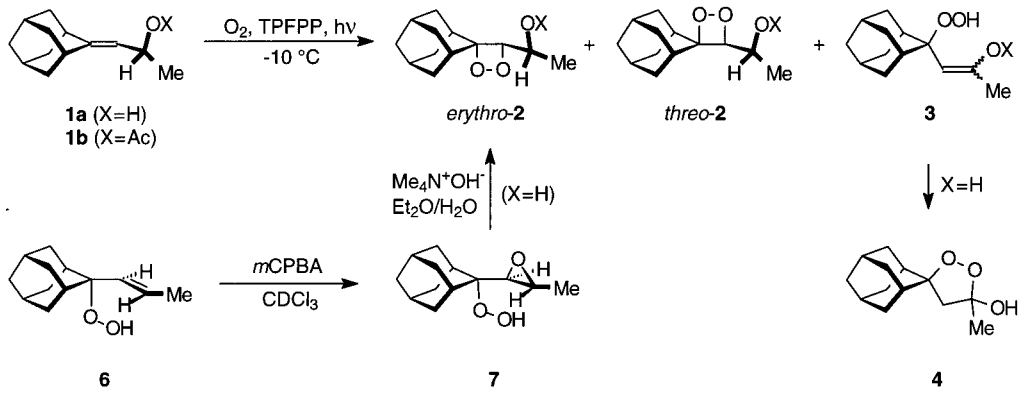
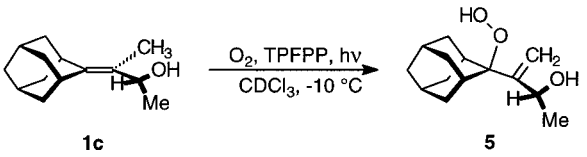


Table 1. Diastereomeric and Mode Selectivities in the Photooxygenation of the Chiral Allylic Alcohol **1a** and Acetate **1b**

		X	solvent[d]	selectivity: diastereo[a] *threo*-**2**: *erythro*-**2**	selectivity: mode[b] [2+2]: ene	convn,[b] %	mb,[b,c] %
1	**1a**	H	$CDCl_3$	≥95:5	47:53[e]	≥ 95	80
2	**1a**	H	CD_3OD/CCl_4 (7:2)	89:11	≥95:5	≥ 95	≥ 95
3	**1b**	Ac	$CDCl_3$	*f*	≤5:95	≥ 95	92
4	**1b**	Ac	CD_3OD	*f*	≤5:95	93	90

[a] Determined by ^{13}C NMR spectroscopy, error was ±5% of the stated value. [b] Determined by ^1H NMR spectroscopy, error was ±5% of the stated value. [c] Mass balance. [d] At −10 °C and 5,10,15,20-tetrakis(pentaflourophenyl)porphine (TPFPP) as sensitizer, except entry 4, at −40 °C with methylene blue. [e] The ene product **3a** was observed as ring tautomer **4** (cf. Scheme 2). [f] No [2+2] cycloaddition was observed.

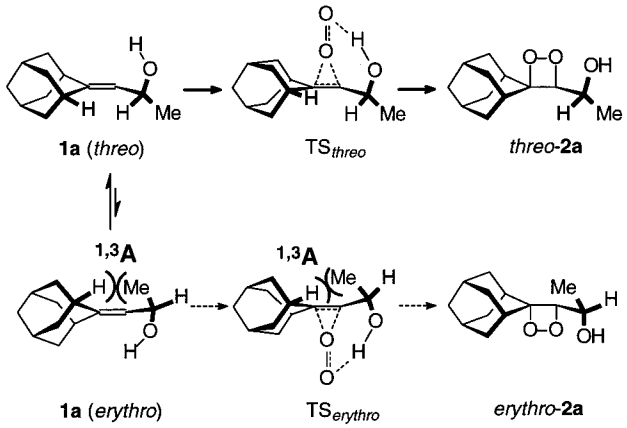
Scheme 3



selectivity for singlet oxygen with this substrate is ca. 50:50. When the allylic alcohol **1a** was photooxygenated in a 7:2 mixture of CD_3OD/CCl_4, the diastereoselectivity for the dioxetanes **2a** dropped to 89:11; no ene product **3a** was formed (Table 1, entry 2). In contrast, in the photooxygenation of the acetate derivative **1b**, only the hydroperoxide **3b** was obtained (Scheme 2), not even traces of the desired dioxetane **2b** were detected in both $CDCl_3$ and CD_3OD (entries 3 and 4 in Table 1). For the methyl-substituted allylic alcohol **1c** (Scheme 3), only the hydroperoxide **5** was obtained, i.e., the ene product of hydrogen abstraction from the allylic methyl group.

The relative configurations of the dioxetanes *threo*-**2a** and *erythro*-**2a** were determined by comparison with authentic *erythro*-**2a**, which was synthesized as shown in Scheme 2. The allylic hydroperoxide **6** was prepared as described[4] and the trans configuration of its double bond was confirmed by the large coupling constant between the olefinic protons (^3J = 15.9 Hz). The epoxidation of the achiral hydroperoxide **6** with *m*CPBA yielded the racemic epoxide **7**, which on base-catalyzed cyclization[5] afforded exclusively the *erythro*-**2a** dioxetane (cf. Scheme 2).

Scheme 4



The very high *threo* selectivity (≥95:5) for the dioxetane formation in the unpolar $CDCl_3$, which is reduced (89:11) in the protic methanol, unequivocally establishes the hydroxy-directing effect also for the [2+2] cycloaddition of singlet oxygen.[1,2] Since experimental and computational studies favor a two-step mechanism for the [2+2] cycloaddition and the ene reaction of singlet oxygen with a common exciplex intermediate,[6] similar hydrogen-bonded transition-state structures must apply for both reaction modes. As shown in Scheme 4, analogous to the ene reaction,[1] 1,3-allylic strain (^{1,3}A) between the methyl group at the chirality center and the allylic hydrogen of the adamantylidene system aligns the molecule conformationally such that the *threo* transition state (TS_{threo}) is favored in energy over the *erythro* one ($TS_{erythro}$). Thus, already in the developing exciplex, the incoming singlet oxygen is attracted through hydrogen bonding by the hydroxy group of the **2a** (*threo*) conformer to afford exclusively the *threo*-**2a** dioxetane (cf. entry 1 in Table 1). Expectedly, in the protic methanol the diastereomeric ratio drops significantly (cf. entry 2 in Table 1) due to the reduced hydrogen bonding between the singlet oxygen and the allylic hydroxy group caused by methanol molecules (intermolecular hydrogen bonding).

Now that we have established that [2+2] cycloaddition of singlet oxygen also takes place *threo*-selectively with chiral allylic alcohols, it is evident that the hydroxy-group directivity of this oxidant is a general phenomenon. This is to say, all three pericyclic reaction modes of singlet oxygen, namely the ene reaction[1] and the [2+2] and the [4+2] cycloadditions,[2] proceed

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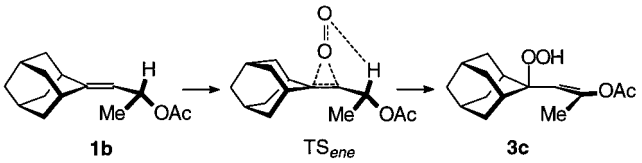
(6) (a) Stratakis, M.; Orfanopoulos, M.; Foote, C. S. *Tetrahedron Lett.* **1996**, *37*, 7159−7162. (b) Yoshioka, Y.; Yamada, S.; Kawakami, T.; Nishino, M.; Yamaguchi, K.; Saito, I. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2683−2699.

Scheme 5



1b TS_{ene} **3c**

through a hydrogen-bonded exciplex. Of course, the geometry of the exciplex is different for the [4+2] cycloaddition (six-centered Diels−Alder arrangement) versus the ene and [2+2] reaction modes (three-centered perepoxide structure). Clearly, hydrogen bonding lowers the energy of the transition state and, thus, accounts for the observed *threo* diastereoselectivity in photooxygenations.

The solvent effect on the mode selectivity is impressive since in $CDCl_3$ about equal amounts of [2+2] and ene reaction are observed, but in methanol exclusively the dioxetane **2a** is obtained (entries 1 and 2 in Table 1). It is a fact that in alcoholic solvents the [2+2] reaction mode is preferred over the ene one due to the more polar dioxetane transition state,[7] but this is so far the most dramatic case. In contrast, most unusual is the mode selectivity observed for the acetate derivative **1b**, since exclusively the ene product is formed in the photooxygenation even in methanol (cf. entries 3 and 4 in Table 1). This expresses once more the importance of hydrogen bonding in the TS_{threo} structure of alcohol **1a** (cf. Scheme 4). For acetate **1b**, such hydrogen bonding is absent and the singlet oxygen coordinates with the allylic hydrogen atom at the acetoxy-bearing chirality center, as shown in the transition state TS_{ene} (Scheme 5). Thus, hydrogen abstraction is favored in the product-determining second step and the [2+2] mode is completely suppressed.

A related mode-selective effect was already reported for the photooxygenation of nonchiral, electron-rich olefins.[8] With heteroatom functionalities, e.g., hydroxy, alkoxy, amino, and amido groups in the allylic position, [2+2] cycloaddition dominated, whereas the corresponding alkyl derivatives yielded appreciable amounts of ene reaction product. The interaction of the heteroatom functionality with singlet oxygen was proposed, which prevents abstraction of the allylic hydrogen atom, and formation of the ene product is circumvented.

Summary

The present results unequivocally illustrate that a strategically placed hydroxy group, conformationally fixed by 1,3-allylic strain directs the incoming singlet oxygen in the [2+2] cycloaddition through hydrogen bonding in the exciplex. Thus, the diastereoselective and mode-controlling hydroxy-group directivity (the synergism between conformational strain and hydrogen bonding) of singlet oxygen is definitely a general phenomenon and operates in all three reaction modes (ene, [2+4], and [2+2]) of the photooxygenation. In this context it should be of mechanistic interest to explore other photochemical reactions.

Experimental Section

General. The elemental analyses were performed at the Microanalytical Department of the Institute of Inorganic Chemistry, University of Würzburg. ^{1}H- and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC 200 or a AC 250 (^{1}H, 200 or 250 MHz; ^{13}C, 50 or 63 MHz) spectrometer by using $CHCl_3$ as standard. The multiplicity of the ^{13}C signals is only given if determined by DEPT spectroscopy. For quantitative NMR analysis, pentachlorobenzene was used as the internal standard. IR spectra were recorded on a FT-IR Perkin-Elmer 1600 spectrophotometer. TLC analysis was conducted on precoated silica gel foils Polygram SIL G/UV254 (40 × 80 mm) from Machery and Nagel. Spots were visualized by UV light or spray tests with phosphomolybdic acid, potassium iodide (for peroxidic compounds), or 2,4-dinitrophenylhydrazone (for carbonyl compounds). Silica gel (20−63 μm, Woelm) was used for flash chromatography.

Materials. *N*-Ethylidene-2-methyl-2-propanamine[9] and *N*-propylidenecyclohexanamine[10] were prepared from the corresponding aldehydes and amines according to literature procedures. The allylic hydroperoxide **6** was synthesized according to literature procedures[4] by addition of propyllithium to tricyclo[3.3.1.1^{3,7}]decanone (adamantanone), followed by elimination of water and subsequent photooxygenation of the resulting alkene.

Tricyclo[3.3.1.1^{3,7}]decylideneacetaldehyde.[11] Under an argon-gas atmosphere, a solution of LDA (120 mmol) in THF (75 mL) was prepared from diisopropylamine and *n*-butyllithium and cooled to −78 °C. A sample of 8.00 mL (5.95 g, 60.0 mmol) of *N*-ethylidene-2-methyl-2-propanamine was added and the resulting mixture was stirred for 30 min, followed by addition of 8.74 mL (60.0 mmol, 10.4 g) of diethyl chlorophosphate. The reaction mixture was stirred for 2 h at −78 °C, allowed to warm slowly to −10 °C, and cooled again to −78 °C, and 6.00 g (40.0 mmol) of tricyclo[3.3.1.1^{3,7}]decanone was added. After keeping the temperature at −78 °C for 30 min, the solution was warmed to 20 °C and stirred for 16 h. A solution of 15.1 g (120 mmol) of oxalic acid in water (150 mL) and toluene (200 mL) were added and the mixture was allowed to stir for 24 h. The phases were separated, the aqueous layer was extracted with ether (2 × 150 mL), and the combined organic phases were washed with a 5% aqueous solution of oxalic acid (2 × 150 mL) and a saturated solution of sodium hydrogen carbonate (2 × 150 mL) and dried over potassium carbonate. After removal of the solvent (60 °C/10 Torr), the residue was purified by silica gel flash chromatography (eluent: petroleum ether/ether 10:1), to yield 2.24 g (32%) of tricyclo[3.3.1.1^{3,7}]decylideneacetaldehyde.

IR (KBr) 2909, 2847 (CH), 1663 (C═O), 1449, 1397, 1349, 1321, 1261, 1195, 1129, 1059, 950, 882, 851; ^{1}H NMR δ 1.7−2.1 (m, 12 H), 2.52 (br s, 1 H), 3.61 (br s, 1 H), 5.79 (d, J = 8.1 Hz, 1 H), 9.99 (d, J = 8.1 Hz, 1 H); ^{13}C NMR δ 27.8 (2×), 33.3, 36.6, 39.6 (2×), 39.9 (2×), 41.5, 121.8, 177.0, 190.0.

2-Tricyclo[3.3.1.1^{3,7}]decylidenepropanal. Under an argon-gas atmosphere, a solution of LDA (60 mmol) in THF (60 mL) was prepared from diisopropylamine and *n*-butyllithium and cooled to −5 °C. A solution of 6.45 g (46.3 mmol) of *N*-propylidenecyclohexanamine in THF (30 mL) was added. After being stirred for 10 min at −5 °C, the mixture was cooled to −70 °C and a solution of 6.96 g (46.3 mmol) of tricyclo[3.3.1.1^{3,7}]decanone in THF (40 mL) was added. The temperature was kept at −70 °C for 3 h, and the mixture was allowed to warm to 20 °C and stirred for another 12 h. A 5% aqueous solution of oxalic acid (125 mL) was added, and the aqueous layer was separated and extracted with ether (2 × 60 mL). The combined organic phases were washed with a 5% aqueous solution of oxalic acid (2 × 60 mL), a saturated solution of sodium hydrogen carbonate (2 × 60 mL), and water (20 mL) and dried over potassium carbonate. Removal of the solvent (10 °C/10 Torr) followed by silica gel flash chromatography (eluent: petroleum ether/ether 10:1) yielded 1.78 g (20%) of 2-tricyclo-[3.3.1.1^{3,7}]decylidenepropanal, mp 72−73 °C, as colorless needles.

IR (KBr) 2999, 2851 (CH), 1664 (C═O), 1614, 1450, 1406, 1371, 1348, 1321, 1284, 1222, 1195, 1103, 1195, 1103, 1060, 1018, 955, 901, 847; ^{1}H NMR δ 1.75 (s, 3 H,), 1.75−2.05 (m, 12 H), 3.04 (br s, 1 H), 3.77 (br s, 1 H), 10.16 (s, 1 H); ^{13}C NMR δ 10.3 (q), 28.2 (2×d), 32.5 (d), 36.1 (d), 37.0 (t), 39.4 (2×t), 40.3 (2×t), 127.1 (s), 171.3 (s),

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190.3 (d). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.74; H, 9.23.

1-Tricyclo[3.3.1.1^{3,7}]decylidene-2-propanol (1a). Under an argon-gas atmosphere, a solution of 1.76 g (10.0 mmol) of tricyclo[3.3.1.1^{3,7}]-decylideneacetaldehyde in dry THF (60 mL) was cooled to −78 °C, and 9.20 mL of a 1.63-M (15.0 mmol) solution of methyllithium in ether were added, and the solution was stirred for 2 h at −78 °C. After warming up to 20 °C, a saturated aqueous solution of ammonium chloride (10 mL) was added. The phases were separated, and the aqueous layer was extracted with ether (2 × 15 mL). The combined organic phases were washed with a saturated solution of sodium hydrogen sulfite (2 × 75 mL), then with a saturated solution of sodium hydrogen carbonate (2 × 75 mL), finally with water (30 mL) and dried over sodium sulfate, and then the solvent was removed (20 °C/10 Torr). Silica gel flash chromatography (eluent: petroleum ether/ethyl acetate 10:1) yielded 1.53 g of **1a** (71%); mp 50−51 °C, as colorless needles.

IR (KBr) 3301 (OH), 2906, 2846 (CH), 1447, 1371, 1320, 1136, 1093, 1056, 945, 857; ^{1}H NMR δ 1.23 (d, J = 6.1 Hz, 3 H), 1.33 (br s, 1 H), 1.55−2.0 (m, 12 H), 2.32 (br s, 1 H), 2.86 (br s, 1 H), 4.62 (dq, J = 8.6 Hz, 6.1 Hz, 1 H), 5.13 (d, J = 8.6 Hz, 1 H); ^{13}C NMR δ 24.2 (q), 28.4 (2×d), 32.8 (d), 37.1 (t), 39.1 (2×t), 39.5 (t), 39.8 (t), 40.2 (d), 63.6 (d), 121.3 (d), 150.3 (s). Anal. Calcd for $C_{13}H_{20}O$: C, 80.83; H, 10.52. Found: C, 81.20; H, 10.48.

3-Tricyclo[3.3.1.1^{3,7}]decylidene-2-butanol (1c). Under an argon-gas atmosphere, 397 mg (2.09 mmol) of 2-tricyclo[3.3.1.1^{3,7}]decylidenepropanal were dissolved in THF (25 mL) and cooled to −70 °C, and 1.92 mL of a 1.63-M (3.13 mmol) solution of methyllithium in ether was added. The solution was stirred for 3 h at −70 °C and finally warmed to 20 °C. A saturated solution of ammonium chloride (6 mL) was added and the phases were separated. The aqueous layer was extracted with ether (2 × 10 mL), the combined organic phases were washed with a saturated solution of sodium hydrogen sulfite (2 × 30 mL), with a saturated solution of sodium hydrogen carbonate (2 × 30 mL), and finally with water (15 mL), and dried over sodium sulfate and the solvent was removed (20 °C/10 Torr). Silica gel flash chromatography (eluent: petroleum ether/ethyl acetate 10:1) yielded 296 mg (75%) of **1c**, mp 95−96 °C, as colorless needles.

IR (KBr) 3341 (OH), 2969, 2918, 2848 (CH), 1449, 1363, 1280, 1188, 1109, 1094, 1081, 1067, 1026, 982, 945, 912, 880, 801; ^{1}H NMR δ 1.21 (d, J = 6.4 Hz, 3 H), 1.27 (br s, 1 H), 1.63 (s, 3 H), 1.55−1.96 (m, 12 H), 2.81 (br s, 1 H), 2.96 (br s, 1 H), 4.90 (q, J = 6.4 Hz, 1 H); ^{13}C NMR δ 21.1 (q), 30.6 (q), 36.0 (d), 39.5 (d), 40.3 (d) 43.4 (t), 44.8 (t), 45.0 (t), 45.2 (t), 45.5 (t), 67.9 (d), 131.8 (s), 146.5 (s). Anal. Calcd for $C_{13}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.25; H, 10.69.

1-Tricyclo[3.3.1.1^{3,7}]decylidene-2-acetoxypropane (1b). To a solution of 401 mg (2.09 mmol) of allylic alcohol **1a** in pyridine (1.5 mL) was added 0.2 mL of acetic anhydride, and the solution was held at reflux for 4 h. The mixture was cooled and added to ice water (10 mL). Ether (5 mL) was added and the system was neutralized with 10% aqueous hydrochloric acid. The phases were separated and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic phases were washed with a saturated solution of sodium hydrogen carbonate (2 × 10 mL) and water (2 × 10 mL) and dried over magnesium sulfate. Removal of the solvent (20 °C/10 Torr) and silica gel flash chromatography (eluent: petroleum ether/ether 30:1) gave 271 mg (59%) of **1b** as a yellow liquid.

IR (film) 2906, 2849 (CH), 1732 (C═O), 1668, 1448, 1369, 1241, 1148, 1099, 1063, 1041, 947, 856; ^{1}H NMR δ 1.26 (d, J = 6.3 Hz, 3H), 1.5−1.9 (m, 12H), 2.01 (s, 3H), 2.32 (br s, 1H), 2.89 (br s, 1H), 5.07 (d, J = 8.7 Hz, 1H), 5.64 (dq, J = 8.7 Hz, 6.3 Hz, 1H); ^{13}C NMR δ 21.5 (q), 28.3 (1×q, 1×d), 32.9 (d), 37.1 (t), 38.7 (1×t, 1×d), 39.0 (t), 39.5 (t), 39.8 (t), 40.2 (d), 67.1 (d), 116.7 (d), 152.6 (s), 171.0 (s). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.55; H, 9.57. Found: C, 76.88; H, 9.46.

2-(*trans*-3-Methyloxiranyl)tricyclo[3.3.1.1^{3,7}]dec-2-yl Hydroperoxide (7). A solution of 207 mg (994 μmol) of (*E*)-2-(1-propenyl)-tricyclo[3.3.1.1^{3,7}]dec-2-yl hydroperoxide (**6**)[4] in $CDCl_3$ (4 mL) was cooled in an ice bath, 209 mg (1.21 mmol) of *m*CPBA was added, and the reaction was monitored by ^{1}H NMR spectroscopy. After 2 h, the solid material was removed by filtration, 500 mg of potassium carbonate was added, and the mixture was stirred for another 1.5 h. After filtration and removal of the solvent (20 °C/10 Torr), the residue was recrystallized from petroleum ether (1 mL) at −50 °C to yield 57.4 mg (26%) of **7** as a colorless powder.

^{1}H NMR δ 1.36 (d, J = 5.0 Hz, 3 H), 1.75−2.10 (m, 12 H), 2.17 (br s, 1 H), 2.48 (br s, 1 H), 3.25−3.45 (m, 2 H), 9.42 (br s, 1 H); ^{13}C NMR δ 27.0, 35.0, 35.1, 38.6, 39.6, 39.9, 40.8, 41.1, 41.2, 44.1, 56.3, 65.8, 80.9.

(*R,*R**)-4-(1-Hydroxyethyl)spiro[1,2-dioxetane-3,2′-tricyclo-[3.3.1.1^{3,7}]decane] (*erythro*-2a).** To a cold (ice bath) solution of 55.1 mg (250 μmol) of the epoxide **7** in ether (2 mL) was added a 25% aqueous solution of tetramethylammonium hydroxide (380 μL, 1.03 mmol). After the solution was stirred for 4 h, the phases were separated and the aqueous layer extracted with ether (3 × 1 mL). The combined organic layers were washed with saturated brine (2 × 2 mL) and dried over sodium sulfate, and the solvent was evaporated (0 °C/10 Torr). Silica gel flash chromatography (eluent: petroleum ether/ethyl acetate 1:1) gave 9.30 mg (17%) of *erythro*-**2a** as a pale yellow oil.

^{1}H NMR δ 1.23 (d, J = 6.1 Hz, 3 H), 1.30−2.30 (m, 16 H), 4.60 (d, J = 9.0 Hz, 1 H); ^{13}C NMR δ 18.2, 25.2, 25.6, 30.6, 31.1, 32.0, 32.9, 35.6, 37.3, 38.7, 46.5, 93.2, 104.6.

General Photooxygenation Procedure. The photooxygenations were performed by passing a gentle stream of dry oxygen gas through a solution of the alkene, which contained ca. 10^{-4} M sensitizer, with simultaneous irradiation by two 150-W sodium lamps. An exact amount of pentachlorobenzene was added as internal standard and the product distribution was determined by ^{1}H NMR analysis.

Photooxygenation of the Allylic Alcohol 1a. A solution of 111 mg (575 μmol) of **1a** and ca. 1 mg of 5,10,15,20-tetrakis(pentafluorophenyl)porphine (TPFPP) as sensitizer in $CDCl_3$ (3 mL) was photooxygenated at −10 °C according to the above general procedure, and the reaction progress was monitored by ^{1}H NMR spectroscopy. After complete conversion (4 h), the solvent was evaporated (0 °C/10 Torr) and the dioxetane *threo*-**2a** and the hydroxydioxolane **4** were separated by low-temperature, silica gel flash chromatography (−20 °C, eluent: petroleum ether/ethyl acetate 10:1).

(*R,*S**)-4-(1-Hydroxyethyl)spiro[1,2-dioxetane-3,2′-tricyclo[3.3.1.1^{3,7}]-decane] (*threo*-2a)**, 13.1 mg (6%), pale yellow oil: R_f (petroleum ether/ethyl acetate 10:1) 0.16; ^{1}H NMR δ 1.22 (d, J = 4.9 Hz, 3 H), 1.50−2.20 (m, 15 H), 2.31 (br s), 4.60 (br s, 1 H); ^{13}C NMR δ 22.3, 25.8, 26.7, 29.3, 31.6, 33.9, 34.3, 35.6, 36.3, 45.2, 90.8, 105.5.

5-Hydroxy-5-methylspiro[1,2-dioxolane-3,2′-tricyclo[3.3.1.1^{3,7}]-decane] (4), 29.0 mg (21%), colorless plates, mp 98−99 °C: R_f (petroleum ether/ethyl acetate 10:1) 0.36; IR (KBr) 3430 (OH), 2907, 2854 (CH), 1703, 1451, 1399, 1270, 123, 1097, 967, 861, 827; ^{1}H NMR δ 1.57 (s, 3 H), 1.60−2.00 (m, 12 H), 2.23 (br s, 1 H), 2.29 (br s, 1 H), 2.44 (d, J = 13 Hz, 1 H), 2.54 (d, J = 13 Hz, 1 H), 2.90 (br s, 1 H); ^{13}C NMR δ 23.1 (q), 25.9 (d), 26.4 (d), 32.8 (t), 33.4 (t), 34.2 (t), 34.8 (d), 36.4 (d), 36.7 (t), 39.0 (t), 55.2 (t), 89.5 (s), 105.6 (s). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.41; H, 8.74.

The photooxygenation of 99.7 mg (518 μmol) of **1a** and ca. 1 mg of TPFPP as sensitizer according to the above procedure in a 7:2 mixture of CD_3OD/CCl_4 (9 mL) at −10 °C yielded only the dioxetanes **2a**; the spectral data of ***threo*-** and ***erythro*-2a** were the same as given above. The diastereomeric ratio was determined on the crude product to be 89:11 in favor of *threo*-**2a** by inverse-gated heteronuclear decoupled ^{13}C NMR spectroscopy.

Photooxygenation of the Allylic Acetate 1b. A solution of 109 mg (465 μg) of **1b** and ca. 1 mg of TPFPP in $CDCl_3$ (5 mL) was photooxygenated at −10 °C for 11 h according to the general procedure to afford the diastereomeric hydroperoxides **3b** in a 1:1 mixture. After removal of the solvent (0 °C/10 Torr), the products were separated by low-temperature, silica gel flash chromatography (−20 °C, eluent: petroleum ether/ether 10:1).

2-(2-Acetoxy-1-propene)tricyclo[3.3.1.1^{3,7}]dec-2-yl Hydroperoxide (3b). (a) Isomer 1: 50.7 mg (41%), colorless oil; ^{1}H NMR δ 1.4−2.1 (m, 14 H), 2.17 (s, 3 H), 2.24 (s, 3 H), 5.19 (1 H), 8.40 (br s, 1 H); ^{13}C NMR δ 20.6, 21.0, 26.7, 27.0, 31.3, 32.1 (2×), 35.1 (2×), 36.5 (2×), 85.5, 119.7, 147.6, 171.8.

(b) Isomer 2: 28.9 mg (23%); colorless needles; mp 96−97 °C; IR (KBr) 3320 (OH), 2940, 2902, 2658 (CH), 1728 (C═O), 1454, 1390, 1374, 1256, 1254, 1131, 1097, 1054, 1034, 984, 924, 883, 866, 834;

^{1}H NMR δ 1.4−1.9 (m, 14 H), 2.01 (s, 3 H), 2.15 (s, 3 H), 5.25 (1 H), 7.94 (br s, 1 H); ^{13}C NMR δ 17.2, 21.0, 26.6, 27.0, 32.0 (2×), 34.3 (2×), 34.5 (2×), 37.5, 85.6, 121.4, 149.3, 195.2. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33. Found: C, 67.37; H, 8.05.

The photooxygenation of a solution of 45.7 mg (195 μmol) of allylic acetate **1b** and ca. 1 mg of methylene blue as sensitizer in CD_3OD (5 mL) at −40 °C was conducted according to the above general procedure. After 10 days, the solvent was removed (0 °C/10 Torr) and the mixture was submitted to NMR analysis.

Photooxygenation of the Allylic Alcohol 1c. A solution of 77.0 mg (373 μmol) of **1c** and ca. 1 mg of TPFPP as sensitizer in $CDCl_3$ (4 mL) was photooxygenated at −10 °C for 1.5 h according to the general procedure to yield exclusively the hydroperoxide **5**. Purification of the product by silica gel flash chromatography (eluent: petroleum ether/ether 1:1) yielded 68.4 mg (77%) of **5**; mp 98−99 °C, as a colorless powder.

IR (KBr) 3376 (OH), 2920, 2855 (CH), 1654, 1450, 1382, 1282, 1084, 1026, 981, 913; ^{1}H NMR δ 1.39 (d, J = 6.4 Hz, 3 H), 1.50−1.95 (m, 12 H), 2.32−2.60 (m, 3 H), 4.54 (dq, J = 3.5 Hz, 6.4 Hz, 1H), 5.44 (s, 1 H), 5.77 (s, 1 H), 7.76 (br s, 1H); ^{13}C NMR δ 22.8, 26.8, 27.6, 30.9, 32.1, 32.4, 32.6, 34.5, 35.0, 37.5, 64.7, 88.4, 107.8, 117.2. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.08; H, 9.06.

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