Synthesis of Optically Pure 3-($^1n\pi^*$)-(1*S*,6*R*)-Bicyclo[4.4.0]decane-3,8-dione, a Molecule Which is Chiral in the Excited State Only

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Abstract: Low-temperature photooxygenation of (1*S*,6*R*)-3-((*E*,*Z*)-methoxymethylene)bicyclo[4.4.0]decan-8-one (**7**), prepared in 10 steps from 2,6-dimethoxynaphthalene (**5**), yields a mixture of four isomeric 1,2-dioxetanes (**8a–d**) with ee > 98%. Upon thermal decomposition, these 1,2-dioxetanes are all precursors for 3-($^1n\pi^*$)-(1*S*,6*R*)-bicyclo[4.4.0]-decane-3,8-dione (**1***), an optically active diketone in its locally excited $^1n\pi^*$ state. The optical activity of this molecule is evidenced by the nonvanishing circular polarization in the chemiluminescence of **8a–d**. The degree of polarization (g_e) at 420 nm equals $-(1.5 \pm 0.3) \times 10^{-3}$, a value which is similar to that of the regular fluorescence of optically active (1*S*,6*R*,8*S*)-8-hydroxybicyclo[4.4.0]decan-3-one (**6**). This similarity implies the absence of substantial racemization in the excited state, whence one concludes that the rate constant for intramolecular $^1n\pi^*$ energy transfer in **1*** is $\lesssim 10^9$ s^{-1}. The chiroptical results show that localization of excitation energy at the carbonyl at the 3-position of **1*** can be achieved by the synthetic route applied, yielding enantiomerically pure 3-($^1n\pi^*$)-(1*S*,6*R*)-bicyclo[4.4.0]decane-3,8-dione (**1***), an optically active molecule whose chirality is due solely to the presence of localized electronic excitation energy.

Introduction

Molecules in which chirality is due solely to small differences between the discriminating groups have always fascinated stereochemists.[1] Striking examples are chiral tetraalkylmethanes[2] and fullerenes[3] and molecules which are chiral due to isotopic substitution.[4] One of the smallest deviations from achirality is found in systems in which the chirality is due solely to the presence of localized electronic excitation energy.[5] This can arise in centrosymmetric or meso compounds with two remote enantiotopic chromophores, as shown in Figure 1 for **1**, **1***, and related structures **2–4**. In the ground state these diketones (*R*,*S*) are achiral, while in the excited state two enantiomeric forms (*R**,*S* and *R*,*S**) are present, provided the excitation energy is localized.

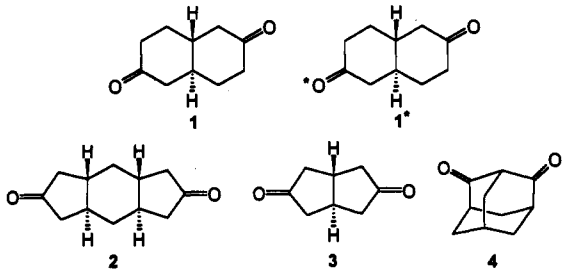

Figure 1. Meso diketones that contain two carbonyl moieties of opposite chirality. All structures are achiral in the ground state but chiral in the excited state, provided excitation energy is localized at one carbonyl group.

The excited state can be formed by the irradiation of *R*,*S* with circularly polarized light. The difference in concentration of *R**,*S* and *S*,*R** is then governed by the dissymmetry factor in absorption ($g_a = \Delta OD/OD$); in fact, the resultant enantiomeric excess (ee) equals $g_a/2$. The optical activity of the excited-state species is evidenced by a nonvanishing degree of circular polarization of luminescence (CPL). Such excited-state chirality has experimentally been demonstrated in the 1,7-diketone **2***.[5] In the case of the 1,5-diketone **3***, a zero CPL has been found which is ascribed to a fast racemization in the singlet excited state (lifetime τ_f) due to $^1n\pi^*$ energy transfer. In the absence of energy transfer, the circular polarization, as measured in these experiments, equals $g_a g_e/2$. Energy transfer reduces the ee, and thus the CPL signal, by a factor of $(2k_{ET}\tau_f + 1)^{-1}$.

Since in photoselection experiments the ee is governed by g_a (which, for the $n \rightarrow \pi^*$ band of ketones, will give an ee of at the most ~10%), a major improvement of selectivity has been foreseen by using chemiexcitation to produce *R**,*S*, potentially with an ee of 100%.[4k,6] According to this approach, singlet-excited-state

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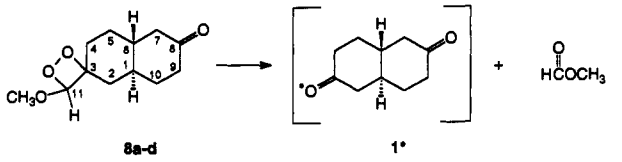
Scheme 1



2,4-adamantanedione (**4***) has been prepared by the thermolysis of the corresponding optically active 1,2-dioxetanes.[6] These four-membered rings are known to dissociate into two carbonyl fragments accompanied with chemiluminescence. Upon thermal decomposition, one of the carbonyls is produced in its (singlet or triplet) excited state by a nonadiabatic process (chemiexcitation). The radiative transition from the singlet excited state to the ground state following chemiexcitation accounts then for the chemiluminescence. Despite the fact that the excitation is directed chemically to one of the carbonyls only, a vanishingly small circular polarization in chemiluminescence of the 1,2-dioxetanes has been detected. A complete loss of optical activity occurred within the lifetime of 2 ns of **4***; due to the close proximity of both carbonyls in **4**, energy transfer is extremely fast.

In this paper we describe the synthesis and the circular polarization of the chemiluminescence of optically pure 3-($^1n\pi^*$)-(1*S*,6*R*)-bicyclo[4.4.0]decane-3,8-dione (**1***),[7] a diketone in which both carbonyls are more remote. The synthetic route is based on our previous work for the chemiexcitation of **4**.[6,8] Via thermal decomposition of the optically active 1,2-dioxetanes **8a–d**, enantiomerically pure **1*** is obtained together with ground-state methyl formate (Scheme 1).

Results and Discussion

Synthesis. The optically active precursor of **1*** is synthesized starting from 2,6-dimethoxynaphthalene (**5**), as outlined in Scheme 2. In six steps and an overall yield of 15%, **5** has been transformed into optically pure (ee > 98%) (1*S*,6*R*,8*S*)-8-hydroxybicyclo[4.4.0]decan-3-one (**6**) using in the last step the HLADH-reduction of **1** as pioneered by Jones et al.[9] The conversion of **6** into (1*S*,6*R*)-3-(*E*,*Z*)-methoxymethylene)bicyclo-[4.4.0]decan-8-one[7] (**7**) is achieved in a four-step procedure. Protection of the alcohol with an acetyl group followed by the Wittig reaction with 1.1 equiv of (methoxymethylene)phosphorane in THF gives the *E*- and *Z*-isomers of (1*S*,6*R*,8*S*)-3-(methoxymethylene)bicyclo[4.4.0]dec-8-yl acetate in a 1:1 ratio in 25% yield. Hydrolysis of the acetyl group with LiOH and a pyridinium chlorochromate oxidation of the alcohol yielded optically pure enol ether (1*S*,6*R*)-**7**. Photooxygenation of **7** with singlet oxygen in dichloromethane at −80 °C, using methylene blue as sensitizer, gives a mixture of four isomeric 1,2-dioxetanes **8a–d** (60%) and allylic hydroperoxides **9a–d** (40%) as byproducts.[8] The ratio of **8** to **9** is strongly influenced by temperature and solvent, as reported for model compounds.[10] The 1,2-dioxetanes are purified (removal of byproducts **9a–d**) by using low-temperature (−30 °C) column chromatography. The four isomeric (1*S*,6*R*)-1,2-dioxetanes **8a–d** are formed in approximately equal amounts by the $^1O_2$ attack of both enol ethers at both sides of the molecule, as is concluded from NMR spectra.

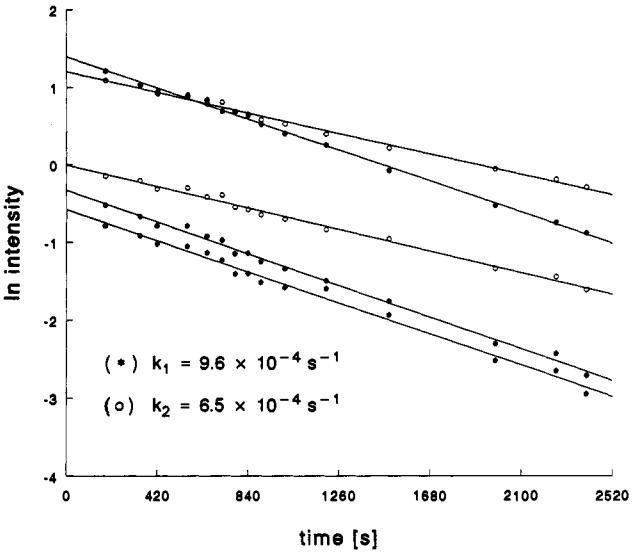


Figure 2. ^1H NMR analysis of the decomposition at 60 °C in toluene-d_8 of the four isomeric 1,2-dioxetanes **8a–d** by monitoring the intensities of the characteristic protons of the four-membered ring. The upper lines represent the methoxy protons, whereas the lower lines represent the olefinic protons. It should be noted that two proton chemical shifts do coincide (line in the middle).

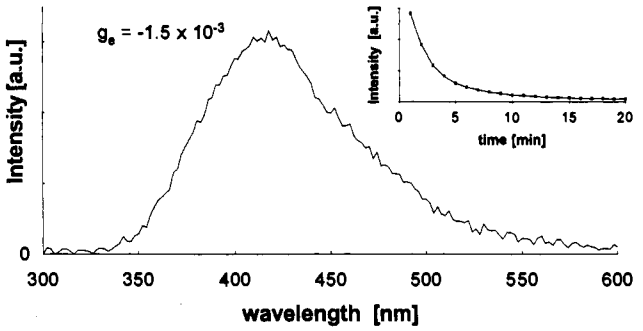


Figure 3. Emission spectrum of the optically active 1,2-dioxetanes during thermolysis in diglyme at 80 °C. The circular anisotropy g_e is detected at optimal wavelength λ = 430 nm. In the inset, the decay of chemiluminescence at 80 °C is shown.

Thermolysis and Chiroptical Properties. In order to investigate the rates of decomposition of the four individual isomeric 1,2-dioxetanes, we have monitored the thermolysis of **8a–d** with ^1H NMR spectroscopy. First-order rate constants of $k_1 = 9.6 \times 10^{-4}$ and $k_2 = 6.5 \times 10^{-4}$ s^{-1} for two pairs of 1,2-dioxetanes are estimated from kinetic studies at 60 °C in toluene-d_8 (Figure 2).

The difference in stability for the two pairs is thought to arise from the difference in steric interactions in the equatorial and axial positions of the oxygen atoms of the four-membered rings, while no difference is expected for the *E*- and *Z*-stereoisomers. The unequal rate constants give rise to a nonexponential decay of the chemiluminescence intensity (Figure 3) as well as the circular dichroism signal at 295 nm (Figure 4). The CD data have been taken on a dilute sample of (1*S*,6*R*)-**8a–d** in bis(2-methoxyethyl) ether (diglyme). After thermolysis at 80 °C, only a trace amount of optically active impurity (probably a trace of ene product) gives rise to a small negative residual CD of **8a–d** at λ_{max} = 295 nm.

The thermolysis of **8a–d** in diglyme at 80 °C is accompanied with chemiluminescent emission, the spectrum of which (Figure 3) closely resembles the fluorescence spectra of **1** and **6**. As expected, $^3n\pi^*$ species formed in the decomposition reaction are effectively quenched under the experimental conditions used.[8]

(7) To obtain as much consistency as possible, numbers in IUPAC nomenclature for the bicyclo compounds are assigned as in **1***, in which priority is given to the carbonyl which is in the $^1n\pi^*$ state.

(8) (a) *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979. (b) Adam, W.; Cilento, G. *Chemical and Biological Generation of Excited States*; Academic Press: New York, 1982. (c) Frimer, A. A., Ed. *Singlet Oxygen*, CRC Press, Inc.: Boca Raton, FL, 1985.

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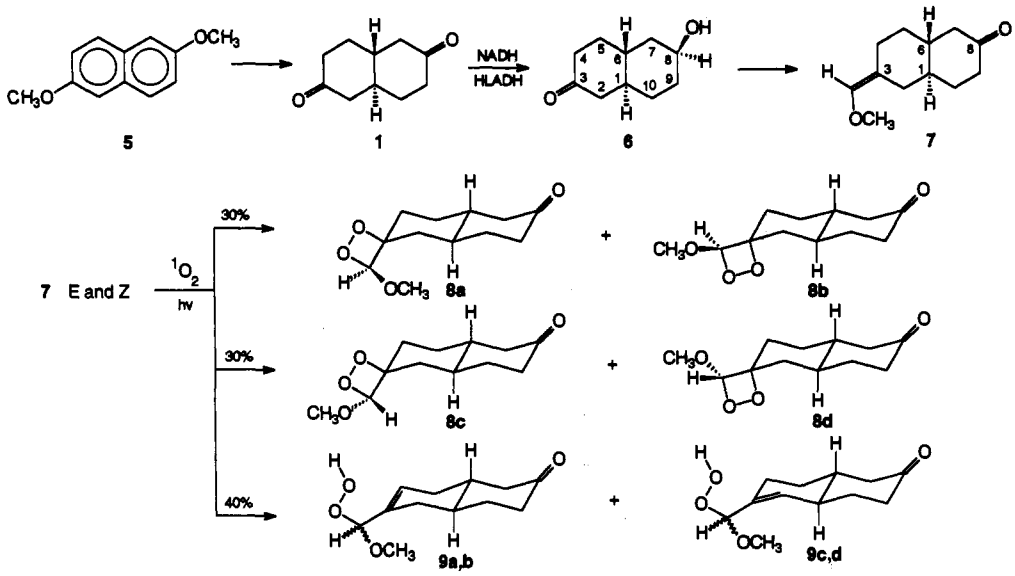
(10) (a) Bartlett, P. D.; Mendenhall, G. D. *Ann. N. Y. Acad. Sci.* **1970**, *171*, 79. (b) Frimer, A. A.; Bartlett, P. D.; Boshung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 7977. (c) Asveld, E. W. H.; Kellogg, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3644. (d) Orfanopoulos, M.; Smonou, I.; Foote, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 3607.

Scheme 2



Collecting the emission at 430 nm, we observe[11] for **8a–d** a dissymmetry factor of chemiluminescence $g_e = -(1.5 \pm 0.3) \times 10^{-3}$. The effect cannot be due to a CD artifact, because in the original sample (i.e., before thermolysis) we observe a zero CD signal at 430 nm.

Thermolysis of the optically active dioxetanes **8a–d** furnishes initially the excited diketone in its locally excited $^1n\pi^*$ state. The optical activity of this molecule is evidenced by the nonvanishing circular polarization in the chemiluminescence. In the absence of racemization, the circular anisotropy in emission of the hydroxy ketone **6**, g_e, should be similar to g_{lum} of the chemiluminescent diketone **1***. The fact that the dissymmetry factor in the chemiluminescence has the same order of magnitude as the dissymmetry factor of the (photoexcited) fluorescence of optically pure hydroxy ketone **6** ($g_e = -(0.9 \pm 0.2) \times 10^{-3}$ at the same wavelength) implies that racemization due to energy transfer is relatively small: $k_{ET} \lesssim 10^9\ s^{-1}$, calculated with $\tau_f = 2$ ns.[12] This result for the 1,6-diketone **1** is in line with the available data on the energy transfer for ketones **2–4**. The distance between both carbonyl carbons in **1**, R_{ab}, as found from X-ray analysis,[13] amounts to 5.25 Å (Figure 5).[14] For the 1,7-diketone **2**, energy transfer is relatively slow ($k_{ET} \lesssim 10^7\ s^{-1}$) for an estimated R_{ab} of 6.95 Å PM3 calculation[15]), while for the 1,5-diketone **3** and the 1,3-diketone **4**, having estimated R_{ab} values of 4.47 and 2.50 Å, respectively, the energy transfer is fast ($k_{ET} \gtrsim 10^{10}\ s^{-1}$).

The chiroptical results indicate that the value of g_{lum} for **1*** is determined only by optical activity due to the presence of a locally excited state in a high enantiomeric excess, equally to the >98% ee and de of the hydroxy ketone **6**.

Concluding Remarks

In conclusion, the results presented in this paper show the successful synthesis and detection of CPL of enantiomerically pure $^1n\pi^*$-excited **1***, whose chirality is due solely to the presence of localized excitation energy. The localization of excitation energy on the carbonyl at the 3-position of **1** has been accomplished by enantioselective chemiexcitation of enol ethers **7** to 1,2-dioxetanes **8a–d**, which by decomposition are all isomeric precursors of 3-(¹nπ*)-**1***. The optical activity was established from the CPL in the chemiluminescence of the 1,2-dioxetanes. No racemization, due to relatively slow intramolecular energy transfer ($k_{ET} \lesssim 10^9\ s^{-1}$) with respect to the singlet-excited-state lifetime (2 ns), was observed. Furthermore, this concept of excited-state chirality of ground-state meso molecules can be used to observe second harmonic generation (SHG) in centrosymmetric molecules and assemblies by using a circularly

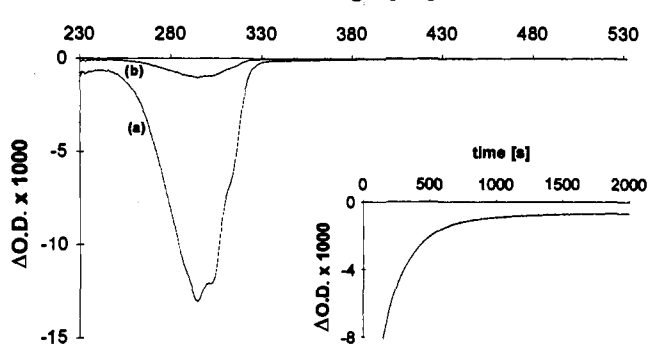


Figure 4. (a) Circular dichroism spectrum of the 1,2-dioxetane showing a negative Cotton effect. (b) The residual CD spectrum after thermolysis at 80 °C in diglyme. In the inset, the decay at 80 °C of the CD signal at 430 nm is shown.

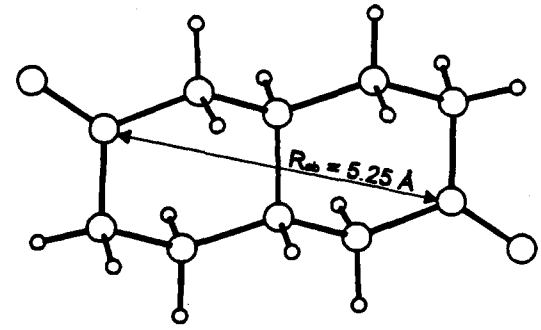


Figure 5. X-ray structure of *trans*-bicyclo[4.4.0]decane-3,8-dione (**1**), showing the distance R_{ab} between the carbon atoms of the two carbonyl groups.

(11) For a description of the instrument, see: Rexwinkel, R. B.; Schakel, P.; Meskers, S. C. J.; Dekkers, H. P. J. M. *Appl. Spectrosc.* **1993**, *47*, 731.
(12) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: California, 1978.
(13) Crystals were obtained from a solution of **1** in tetrahydrofuran by slow evaporation. Details of crystal structure analysis are available on request and are to be published. X-ray analysis was performed by A. Schouten and J. Kroon, Bijvoet Center for Biomolecular Research, Padualaan 8, 3584 CH Utrecht, The Netherlands.
(14) The preliminary refinement $R_{ab} = 5.248$ Å in the X-ray analysis of **1**, which crystallizes in the monoclinic spacegroup $P2_1/n$ (No. 14), confirms the structure. Crystal data: $a = 5.2490(1)$, $b = 10.6801(3)$, and $c = 7.9484(2)$ Å, $\beta = 96.901(2)°$; $Z = 2$.
(15) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

polarized fundamental beam. Following these lines, we have observed already SHG in centrosymmetric crystals of a racemic mixture;[16] design of other systems with localized distortion of centrosymmetry by excitation is in progress.

Experimental Section

General Techniques. Melting points were determined on a Unicam THMS heating apparatus. Infrared (FT-IR) spectra were recorded on a Perkin-Elmer 1605 FT-IR spectrophotometer. CD spectra were recorded on a Jasco spectropolarimeter J600. UV spectra were recorded on a Perkin-Elmer UV/vis spectrophotometer Lamba 3B. Elemental analyses were performed on a Perkin-Elmer 240 apparatus. Optical rotations were measured on a Optical Activity Ltd. AA10 polarimeter. Proton, deuterium, and carbon-13 NMR spectra were recorded on a Bruker AM400 spectrometer using tetramethylsilane (TMS, 0 ppm) as internal standard. GC analyses were carried out on a Kipp Analytica 8200 instrument with FID detection (25 m × 0.25 mm i.d., column type WCOT fused silica, stationary phase CP SIL-5 CB, film thickness 0.25 μm). Chemiluminesence spectra were recorded on a Spex Fluorolog II emission spectrometer.

Circular Polarization of Luminescence. Measurements of the circular polarization of the luminescence (CPL) and chemiluminescence were performed at Leiden University on a custom-built spectrometer operating in the photon counting mode. A detailed description of the instrument has been published.[11] The measurements were performed on ~0.05 M solutions in spectrometric grade CH_3CN for **6** and bis(2-methoxyethyl) ether for **1***. The bandwidth of the emission channel was chosen to be 30 nm.

Materials. Column chromatography was performed using Merck silica gel 60, 230–400 mesh as the stationary phase. Analytical thin-layer chromatography was conducted on precoated TLC plates, silica gel 60, F-254 layer thickness 0.25 mm, using UV (254 nm) and iodine detection. Preparations of dioxetanes were carried out in a 700-mL reaction vessel. All solvents and commercial reagents were reagent grade. Diethyl ether was dried over $CaCl_2$ and stored over sodium wire. Dichloromethane was distilled from CaH_2, pyridine from KOH pellets. Oxygen was dried over several traps, one containing concentrated sulfuric acid and two KOH pellets. Tetrahydrofuran (THF) was distilled under dry argon from sodium in the presence of benzophenone.

(1*S*,6*R*)-Bicyclo[4.4.0]decane-3,8-dione (1). *trans*-Bicyclo[4.4.0]-decane-3,8-dione (**1**) was prepared according to literature procedures.[9a] Crystals (for X-ray analysis) were obtained from a solution of **1** in tetrahydrofuran by slow evaporation,[13,14] mp 137.5–138 °C (lit.[9a] mp 138 °C). ^{1}H NMR ($CDCl_3$): δ 2.45–2.55 (2H, m, H_2, H_7), 2.30–2.45 (4H, m, H_4, H_9), 2.08–2.20 (2H, dd, H_2, H_7), 2.00–2.08 (2H, m, H_1, H_6), 1.75–1.90 (2H, m, H_1, H_6), 1.50–1.65 (2H, m, H_5, H_{10}). ^{13}C NMR ($CDCl_3$): δ 209.86 (s, C_3, C_8), 47.08 (t, C_2, C_7), 41.44 (d, C_1, C_6), 40.27 (t, C_4, C_9), 33.06 (t, C_5, C_{10}). IR (KBr): ν 1710 (C=O stretch, saturated). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.44; H, 8.46.

(1*S*,6*R*,8*S*)-8-Hydroxybicyclo[4.4.0]decan-3-one (6). This compound was prepared according to ref 9b. A 0.1 M phosphate buffer (400 mL, pH 6.5), prepared from 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 solutions of Millipore water, was sterilized for about 30 min. Diketone **1** (1 g, 6.02 mmol), NAD^+ (700 mg), ethanol (6 mL), and HLADH (140 units) were added to the buffer, and the mixture was kept in the dark at room temperature. After 8 days maximum reaction time, the mixture was worked up by saturation with NaCl, extraction with $CHCl_3$ (4 × 50 mL), and rotary evaporation of the dried ($MgSO_4$) $CHCl_3$ solution. The crude product mixture was chromatographed on silica gel (dichloromethane/ethyl acetate, 60:40 elution) to give the pure hydroxy ketone product **6** (680 mg, yield 67%) as a white solid (unreacted diketone was recovered), mp (after crystallisation from ethyl acetate) 77–79 °C (lit.[9b] mp 77–79 °C), $[\alpha]^{25}_D$ = +24.5° (*c* 0.7, ethanol). ^{1}H NMR ($CDCl_3$): δ 4.20 (1H, m, H_8), 1.20–2.40 (14H, m). ^{13}C NMR ($CDCl_3$): δ 211.55 (s, C_3), 66.13 (d, C_8), 48.25 (t, C_2), 42.90 (d, C_1), 41.61 (t, C_4), 38.80 (t, C_7), 34.80 (d, C_6), 33.31 (t, C_5), 32.00 (t, C_{10}), 27.55 (t, C_9). IR (KBr): ν 3505 (–OH, broad), 1699 (C=O stretch, saturated). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 8.59. Found: C, 71.49; H, 8.82.

(1*S*,6*R*,8*S*)-8-Acetylbicyclo[4.4.0]decan-3-one. To a solution of **6** (1.5 g, 8.92 mol) in dry pyridine (18 mL, 0.22 mol) was added 2.5 mL of acetic anhydride (26.8 mmol). After being stirred for about 15 h at room temperature, the reaction mixture was poured into water (100 mL) and extracted with hexane/ether (1:1) (4×, 30 mL). The combined organic layers were washed again with water (2×, 10 mL), dried ($MgSO_4$), concentrated in vacuo, and coevaporated with toluene and methanol, respectively, to give (1*S*,6*R*,8*S*)-8-acetylbicyclo[4.4.0]decan-3-one as a colorless oil (1.71 g, yield 91%). ^{1}H NMR ($CDCl_3$): δ 5.1 (1H, br, H_8), 2.2–2.4 (3H, m), 2.0 (3H, s, CH_3), 1.80–1.95 (3H, m), 1.6–1.75 (1H, m), 1.25–1.50 (5H, m), 1.10–1.25 (1H, m). ^{13}C NMR ($CDCl_3$): δ 210.55 (C_3), 170.08 (OCO), 69.13 (C_8), 47.79, 42.13, 41.16, 35.66, 35.23, 32.78, 28.75, 27.90, 21.12. IR (neat): ν 1731 (–CO—O– stretch, saturated), 1715 (C=O stretch, saturated), 1367 (O=C—CH_3 deformation), 1240 (O—C=O stretch).

(1*S*,6*R*,8*S*)-3-((*E*,*Z*)-Methoxymethylene)bicyclo[4.4.0]dec-8-yl Acetate. To a stirred suspension of (methoxymethyl)triphenylphosphonium chloride (4.24 g, 12.4 mmol) in 35 mL of anhydrous THF in a nitrogen atmosphere was added 3.8 mL of 2.5 M *n*-butyllithium (9.52 mmol), whereupon the deep red color of the ethylidenephosphorane was produced. After the mixture was stirred for about 1 h, a solution of (1*S*,6*R*,8*S*)-8-acetylbicyclo[4.4.0]decan-3-one (2.0 g, 9.52 mmol) in anhydrous THF was added rapidly to the dark red solution. After the solution was stirred for another 2 h at room temperature, 10 mL of a saturated ammonium chloride solution was added. The reaction mixture was diluted with diethyl ether (250 mL) and washed with water (3 × 20 mL). Extraction with ether, drying ($MgSO_4$), and rotary evaporation of the organic layer afforded a dark red residue. Column chromatography on silica gel (hexane/ethyl acetate, 92:8 elution) gave 1.25 g of (1*S*,6*R*,8*S*)-3-((*E*,*Z*)-methoxymethylene)bicyclo[4.4.0]dec-8-yl acetate as a colorless oil (yield 55%). ^{1}H NMR ($CDCl_3$): δ 5.8 (2H, s, H_{11}), 5.1 (2H, br, H_8), 3.55 (6H, d, OCH_3), 2.75–2.85 (1H, dd, H_2), 2.65–2.75 (1H, m, H_4), 2.05 (6H, s, CH_3), 0.9–2.1 (26H, m). ^{13}C NMR ($CDCl_3$): δ 170.41 (s, O—C=O), 139.01 (d, C_{11}), 138.89 (d, C_{11}), 117.24 (s, C_3), 117.17 (s, C_3), 69.99 (d, C_8), 59.11 (q, OCH_3), 43.82, 42.53, 37.02, 36.98, 36.92, 36.83, 34.84, 33.49, 31.91, 29.94, 29.71, 29.64, 27.90, 27.74, 24.86, 21.32. IR (neat): ν 2839 (–O—CH_3, C—H stretch), 1735 (–CO—O– stretch, saturated), 1687 (C=C stretch), 1364 (O=C—CH_3 deformation), 1245 (O—C=O stretch).

(1*S*,6*R*,8*S*)-3-((*E*,*Z*)-Methoxymethylene)bicyclo[4.4.0]decan-8-ol. To a solution of (1*S*,6*R*,8*S*)-3-((*E*,*Z*)-methoxymethylene)bicyclo[4.4.0]dec-8-yl acetate (1.5 g, 6.29 mmol) in 30 mL of ethanol was added 15 mL of an aqueous solution of lithium hydroxide (1 g, 24 mmol). The mixture was stirred for 16 h and then diluted with 250 mL of dichloromethane. The organic layer was washed with water, dried ($MgSO_4$), and rotary evaporated to give (1*S*,6*R*,8*S*)-3-((*E*,*Z*)-methoxymethylene)bicyclo-[4.4.0]decan-8-ol as a colorless oil (1.17 g, yield 95%). The reaction was monitored by TLC (hexane/ethyl acetate, 80:20 elution), R_f = 0.15, $[\alpha]^{25}_D$ = –28.8° (*c* 0.052, EtOH). ^{1}H NMR ($CDCl_3$): δ 5.8 (2H, s, H_{11}), 3.55 (6H, d, OCH_3), 2.85–2.9 (1H, dd, H_4), 2.75–2.85 (1H, m, H_4), 1.0–2.4 (24H, m). ^{13}C NMR ($CDCl_3$): δ 138.86 (d, C_{11}), 138.76 (d, C_{11}), 117.75 (s, C_3), 117.68 (s, C_3), 66.61 (d, C_8), 66.57 (d, C_8), 59.19 (q, OCH_3), 44.26, 42.95, 39.89, 39.83, 37.16, 36.31, 36.27, 35.05, 33.72, 32.61, 32.52, 32.05, 30.08, 27.30, 27.15, 25.00. IR (neat) ν 3360 (–OH, broad), 2839 (–O—CH_3, C—H stretch), 1686 (C=C stretch).

(1*S*,6*R*)-3-((*E*,*Z*)-Methoxymethylene)bicyclo[4.4.0]decan-8-one (7). To a stirred solution of (1*S*,6*R*,8*S*)-3-(methoxymethylene)bicyclo[4.4.0]-decan-8-ol (1.3 g, 6.62 mmol) in 40 mL of dry dichloromethane in a nitrogen atmosphere was added in small portions 1.4 g (5.3 mmol) of pyridinium chlorochromate (PCC). The reaction was monitored with TLC (eluent ethyl acetate/hexane, 20:80), R_f = 0.25, and after 1 h another 0.35 g (1.4 mmol) of PCC was added. After another hour, the reaction mixture was poured into 100 mL of dry diethyl ether. The dark brownish residue was washed with dry diethyl ether (2 × 30 mL), and the ether layer was decanted. The collected ether layers were filtered over $MgSO_4$ and Florisil (mesh 600) and then rotary evaporated. The crude product obtained was purified by chromatography on silica gel (hexane/ethyl acetate, 80:20) to give (1*S*,6*R*)-3-((*E*,*Z*)-methoxymethylene)bicyclo-[4.4.0]decan-8-one (**7**) as a colorless oil (700 mg, yield 54%), $[\alpha]^{25}_D$ = –54.5° (*c* 0.213, EtOH). This product was stored in the freezer since it readily hydrolizes to aldehyde derivatives. ^{1}H NMR ($CDCl_3$): δ 5.8 (2H, br, H_{11}), 3.55 (6H, d, OCH_3), 2.85–2.95 (1H, dd, H_2), 2.75–2.85 (1H, m, H_4), 1.0–2.4 (26H, m). ^{13}C NMR ($CDCl_3$): δ 211.31 (C_8), 139.59 (C_{11}), 139.49 (C_{11}), 116.25 (C_3), 116.13 (C_3), 59.30 (OMe), 48.24, 48.16, 43.20, 42.88, 41.61, 41.24, 41.18, 36.19, 35.35, 34.03, 33.23, 33.16, 31.05, 29.15, 24.08. IR (neat): ν 2837 (–O—CH_3, C—H stretch), 1713 (C=O stretch, saturated), 1687 (C=C stretch).

1,2-Dioxetanes of 3-((*E*,*Z*)-methoxymethylene)bicyclo[4.4.0]decan-8-one (8a–d). Compound **7** (700 mg 3.5 mmol) and sensitizer methylene

(16) (a) Meijer, E. W.; Havinga, E. E.; Rikken, G. L. J. A. *Phys. Rev. Lett.* **1990**, *65*, 37. (b) Meijer, E. W.; Havinga, E. E. *Synth. Met.* **1993**, *57*, 4010.

blue (10 mg) were dissolved in 600 mL of dichloromethane and photooxygenated for 1 h at −80 °C. The irradiations were carried out with a Hanau TQ78 500-W medium-pressure mercury lamp through quartz, using a sheet of brownish polyimide (Kapton 500H, du Pont de Nemours) wrapped around the lamp compartment as short wavelength filter (cutoff 550 nm). Cooling of the lamp and primary cooling of the reaction vessel were accomplished by means of a closed circuit filled with methanol from a cryostat. The temperature of −80 °C was reached by extra external cooling baths of ethanol and liquid nitrogen. Column chromatography at −30 °C using dichloromethane/ethyl acetate, 60:40 elution, resulted in removal of the sensitizer, yielding a mixture of dioxetanes and allylic hydroperoxides in a ratio of 60:40. Pure dioxetane was obtained by concentrating 700 mL of the crude dioxetane solution to ≈250 mL and subsequent column chromatography at −30 °C using dichloromethane/acetone, 96:4 as eluent. The relatively low-boiling solvents, dichloromethane, acetone, and ethyl acetate, were removed in the presence of an appropriate high-boiling solvent, bis(2-methoxyethyl) ether (diglyme) or toluene-d_8. CPL measurements were carried out using a concentrated dioxetane solution (a solution of 550 mL of 1,2-dioxetane was concentrated into 20 mL of diglyme). For recording ^{1}H and ^{13}C NMR spectra, an aliquot of the dioxetane solution was concentrated at 0 °C. During evaporation, cold $CDCl_3$ or toluene-d_8 was added in such a way that the 1,2-dioxetane was always present in solution. The 1,2-dioxetane was stored as a solution in dichloromethane below −20 °C. ^{1}H NMR (toluene-d_8, T = 25 °C): δ 5.26, 5.22, 5.20, 5.18 (4 × 1H, s, H_{11}), 3.28, 3.26 (2 × 3H, s, OCH_3), 3.16 (6H, s, OCH_3), 2.7–0.7 (envelope). ^{13}C NMR ($CDCl_3$, T = −20 °C): δ 211.28, 211.08 (s, 2 × C_8), 109.60, 109.44 (d, 2× C_{11}), 89.54, 89.51, 89.43, 89.34 (s, 4× C_3), 56.04, 55.99, 55.69, 55.62 (q, 4× OCH_3), 47.98, 47.25, 46.91, 46.74 (t, 4× C_7), 41.16, 40.92, 40.67, 40.52, 40.16, 40.92, 40.67, 40.06, 39.37, 38.02, 37.11, 35.70, 35.38, 34.94, 33.79, 33.52, 32.64, 32.44, 32.28, 30.23, 29.2, 28.04, 27.7, 26.27.