Photooxygenation of 2,4-Dimethyl-1,3-pentadiene: Solvent Dependence of the Chemical (Ene Reaction and [4 + 2] Cycloaddition) and Physical Quenching of Singlet Oxygen

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The photooxygenation of 2,4-dimethyl-1,3-pentadiene (**1**) was investigated in seven polar and nonpolar solvents by oxygen-uptake measurements. The overall deactivation rate k_o (= $k_r + k_q$) was additionally measured in chloroform solutions by singlet-oxygen ($^1\Delta_g$) phosphorescence quenching which showed excellent agreement with the data from the detailed steady-state kinetics. The difference in solvent-polarity effects on the [4 + 2] cycloaddition (major path, leading to the endoperoxide **2**) and ene reaction (minor path, leading to the allylic hydroperoxide **3**) are explained by competition between a concerted and a perepoxide mechanism. In all solvents the physical quenching of singlet oxygen by **1** is at least as efficient as the chemical quenching. The reaction of the endoperoxide **2** and 3,3,6,6-tetramethyl-1,2-dioxene **9** with carbonyl compounds in the presence of TMSOTf resulting in the dihydrofuran **8** and the 1,2,4-trioxane **10**, was also studied.

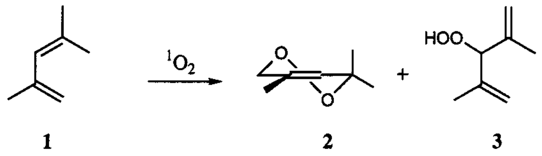
Introduction

Molecular oxygen in its first excited singlet state (a$^1\Delta_g$-$^1O_2$) is a highly reactive molecule and is quenched by many organic compounds either physically (i.e. by energy or electron transfer) or by a chemical reaction.[1] The most important reaction pathways with unsaturated organic substrates are the ene reaction[2] and the [4 + 2][3] and [2 + 2] cycloaddition[4]. In order to examine the synthetic potential of this simplest possible activated oxygen-transfer reagent, we are currently investigating the dependence of the different deactivation modes on the structural features of the substrates and the reaction medium. In this context we are especially interested in substituent effects on the physical quenching of $^1O_2$ by alkenes and dienes.[5] This aspect has often been ignored in the analyses of $^1O_2$ reactivity for synthetic applications, where only the kinetics of product formation (i.e. k_r) were determined. Because $^1O_2$ is an electronically excited molecule, the physical quenching process can also contribute to selectivity effects in photooxygenation reactions, i.e. chemo-, regio-, and diastereoselectivity can originate from a combination of chemical and physical quenching. Especially the work by Adam and co-workers on hydroxy-directing effects in ene reactions[6] and [4 + 2] cycloadditions[7] as well as by Stephenson and Orfanopoulos on the "*cis* effect"[8] and the "large-group effect"[9] in ene reactions deserve more elaborate investigations into the interplay of several possible quenching mechanisms. We have reported earlier the detailed reaction kinetics of the photooxygenation of 2,4-hexadienes[10] and 2,5-dimethyl-2,4-hexadiene[11] in several solvents. Herein we describe our results obtained with 2,4-dimethyl-1,3-pentadiene (**1**) as singlet-oxygen acceptor.

Product Analysis and Determination of Product Ratios

The photooxygenation of **1** in all solvents investigated resulted in two products: the endoperoxide **2** and the allylic hydroperoxide **3** (Scheme 1). No trace of [2 + 2] cycloaddition products or the corresponding decomposition products (carbonyl compounds) were detected. The product ratios were determined by ^1H-NMR spectroscopy of the crude reaction mixtures and are summarized in Table 1. As characteristic signals the methyl resonances at $\delta = 1.26$ (for **2**) and 1.70 (for **2** and **3**) were used. The endoperoxide **2**[12] was isolated from the tetrachloromethane photooxygenation [with tetraphenylporphin (TPP) as sensitizer] in 91% yield, the allylic hydroperoxide **3** from the methanol photooxygenation [with Rose bengal (RB) as sensitizer] in 16%

Scheme 1. Photooxygenation of **1**



1434−193X/98/1212−2833 $ 17.50+.50/0

yield by distillation from the crude reaction mixtures. For **2** low-temperature NMR investigations were repeated[12] and resulted in coalescence temperatures (300 MHz) of 210 K (for methyl resonances) and 220 K (for methylene resonances). From these data an activation energy of 11.2 ± 0.5 kcal/mol for the chair-chair conversion of the endoperoxide **2** was calculated.

Table 1. Product distribution[a] of singlet-oxygen reactions with **1**

	2 (%)	**3** (%)
CCl_4/TPP	97	3
C_6H_6/TPP	95	5
$CHCl_3$/TPP	92	8
CH_2Cl_2/TPP	89	11
$(CH_3)_2CO$/RB	84	16
CH_3OH/RB	65	35
CH_3CN/RB	81	19

[a] By ^{1}H-NMR integration of the crude product mixtures.

Determination of Quenching and Reaction Rates: Oxygen Uptake Analysis

Chemical and physical quenching processes can be separately analyzed by steady-state methods with oxygen-uptake measurements. The algorithm used to extract the rate constants is described in detail in ref.[11]. As standard, 2,5-dimethylfuran (DMF) was used, a singlet-oxygen acceptor which yields only one primary product in all solvents with negligible physical quenching[13]. When applied in concentrations higher than 2×10^{-4} M the rate of oxygen consumption v_{DMF} is independent of the acceptor concentration and thus represents the limiting oxygen-consumption rate. By measuring the rate of oxygen consumption by the acceptor molecule v_A the dependence of the ratio v_{DMF}/v_A on the acceptor concentration was determined. This fraction is expressed by eq. 1

$$v_{DMF}/v_A = (1 + k_q{}^A/k_r) + (k_d/k_r + k_q{}^S[\mathrm{Sens}]/k_r)\,[A]^{-1} \qquad (1)$$

in which $k_q{}^A$ = physical quenching of singlet oxygen by the acceptor, k_r = chemical quenching (= reaction) of singlet oxygen by the acceptor, k_d = solvent quenching (= 1/lifetime), and $k_q{}^S$ = physical quenching of singlet oxygen by the sensitizer.

By plotting v_{DMF}/v_A versus the inverse acceptor concentration the value of $1 + k_q{}^A/k_r$ was determined from the intercept and $(k_d/k_r + k_q{}^S[\mathrm{Sens}]/k_r)$ from the slope. If v_{DMF}/v_A is independent of the sensitizer concentration, this slope equals k_d/k_r and k_r can be directly calculated (likewise $k_q{}^A$ from the intercept). If, however, the slope of eq. 1 depends on the sensitizer concentration, a plot of the different slopes of eq. 1 versus the corresponding sensitizer concentrations leads to the $k_q{}^S$ values which are used to solve eq. 1 and determine the so-called β values (= k_d/k_r). In order to resolve the equations, reliable numbers for the solvent deactivation rates k_d are needed. The lifetime of singlet oxygen in different solvents has been measured over the last twenty years by a large number of research groups using different methods. For the steady-state analyses we applied the lifetimes published by Merkel and Kearns[14] in order to have a comparable data set for evaluation of the reaction rate constants. For benzene and chloroform we used lifetimes published by Schmidt and Afshari[15] which deviate slightly but are more accurate. By variation of the sensitizer concentrations and extrapolation to zero, the quenching rate of singlet oxygen by the dyestuff was obtained. Only for tetraphenylporphin (TPP) in chlorinated solvents, a pronounced dependence of v_A from the sensitizer concentration was detected. That porphyrins do quench singlet oxygen to an appreciable extent also has been reported by others and a rate constant for the $^1O_2$ quenching by TPP in CCl_4 of 7.0×10^5 $\mathrm{M^{-1}s^{-1}}$ was reported.[16] From our measurements higher quenching rates resulted ($1.7 \pm 0.3 \times 10^7$ $\mathrm{M^{-1}s^{-1}}$ for the chlorinated solvents CCl_4, $CHCl_3$, and CH_2Cl_2). Even higher quenching rates were reported by Tanielian et al. for the singlet-oxygen quenching by hematoporphyrins (ca. 5×10^8 $\mathrm{M^{-1}s^{-1}}$).[17] The data for physical quenching by the sensitizer and for physical and chemical quenching by the acceptor **1** are summarized in Table 2.

Singlet Oxygen Phosphorescence Analysis

From the oxygen-uptake kinetics we calculated an overall quenching rate k_o (= $k_r + k_q$) of 8.2×10^5 l/mol s in $CHCl_3$. In order to evaluate the quality of our method and to compare the data obtained with modern singlet-oxygen luminescence-detection methods, we determined the phosphorescence quenching in chloroform solutions using py-

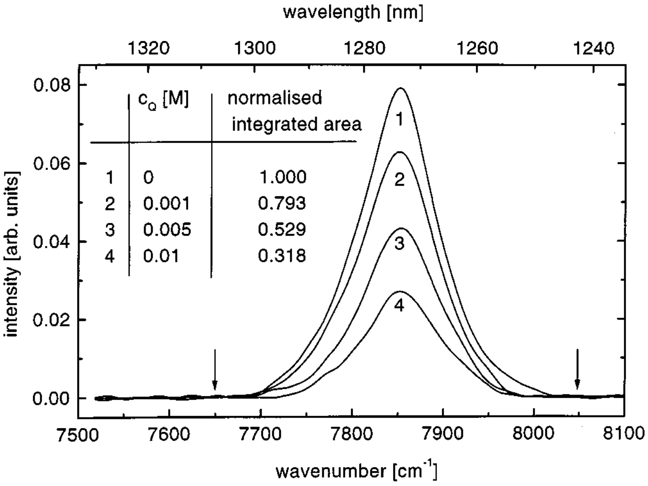
Table 2. Absolute rate constants for the photooxygenation of **1**

	k_o (× 10^5)[a]	$k_q{}^A$ (× 10^5)[a]	k_{4+2} (× 10^5)[a]	k_{ene} (× 10^5)[a]	$k_q{}^S$ (× 10^7)[a]	(ε − 1)/(2ε + 1)	k_d (× 10^4)[b]
CCl_4/TPP	9.34	4.45	4.74	0.15	1.38	0.222	0.14
C_6H_6/TPP	17.3	12.6	4.22	0.22	−	0.232	3.20
$CHCl_3$/TPP	8.20	4.72	3.21	0.28	1.57	0.356	0.44
CH_2Cl_2/TPP	11.79	5.52	5.58	0.69	2.01	0.420	0.95
$(CH_3)_2CO$/RB	15.34	6.42	7.49	1.43	−	0.465	3.80
CH_3OH/RB	27.93	14.6	10.8	2.53	−	0.477	14.30
CH_3CN/RB	19.14	9.37	6.25	3.52	−	0.480	3.30

[a] In l/mol s, determined by steady-state kinetic analysis using 2,5-dimethylfuran as reaction standard and corrected for sensitizer quenching in cases of the chlorinated solvents ($k_o = k_q{}^A + k_{4+2} + k_{ene}$). − [b] Solvent quenching rate in $\mathrm{s^{-1}}$ from ref.[14], for $CHCl_3$ and benzene from ref.[15].

rene as singlet-oxygen sensitizer. The singlet-oxygen phosphorescence quantum yield in chloroform has been determined to 3.6 ± 1.4 × $10^{-4[18]}$. In spite of this low efficiency we were able to measure the phosphorescence spectra of O_2 ($a^1\Delta_g \rightarrow X^3S_g^-$ transition) with high signal-to-noise ratio by irradiating air-saturated solutions of pyrene (10^{-3} M) in $CHCl_3$ containing different concentrations of **1** (Figure 1).

Figure 1. Singlet-oxygen phosphorescence spectra in the absence and presence of **1**



The region of the spectra used for integration is marked with arrows in the spectra of Figure 1. Normalized integrated areas of the phosphorescence spectra are also listed in Figure 1. In analogy to the work by Wessels and Rodgers[19], we used the Stern-Volmer equation

$$\phi_0/\phi = 1 + k_o \times \tau \times c_Q \qquad (2)$$

in which τ is the lifetime of $^1O_2$ ($a^1\Delta_g$), ϕ_0 the integrated area of phosphorescence in the absence of the quencher (τ taken from ref.[15] to be 2.3 × 10^{-4} s), ϕ the integrated area of phosphorescence in the presence of the quencher, and c_Q the quencher concentration (in M); an overall quenching (physical and chemical) rate k_o of 9.1 ± 0.6 × 10^5 M^{-1} s^{-1} is derived (Figure 2). Thus, the two methods which were applied are in excellent agreement with each other (approx. 15% deviation).

Figure 2. Stern-Volmer plot

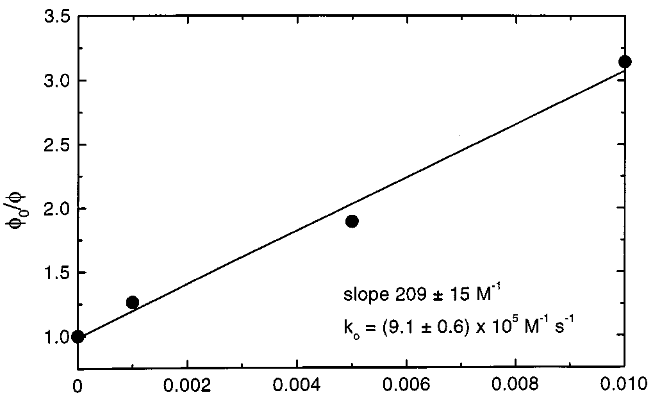


Figure 3. Solvent dependence of physical quenching and ene reaction

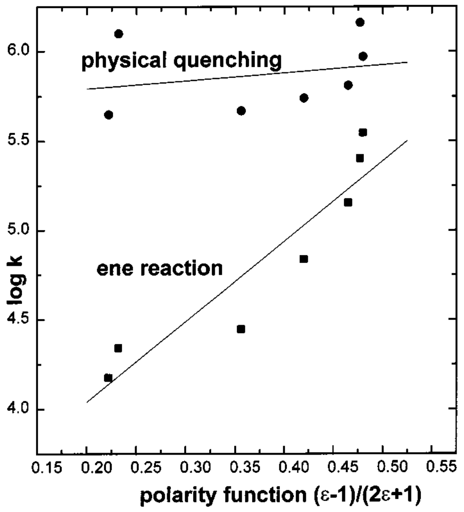
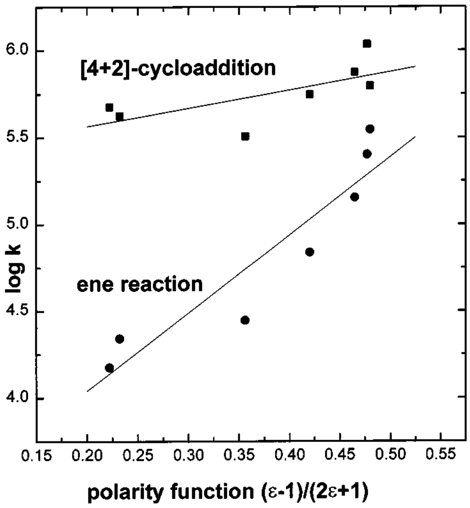


Figure 4. Solvent dependence of [4 + 2] cycloaddition and ene reaction



Discussion of Reaction Rates

Analysis of the kinetic data summarized in Table 2 reveals that the rates for physical quenching of $^1O_2$ by the acceptor molecule **1** as well as for the [4 + 2] cycloaddition are nearly independent of the solvent polarity (see Figures 3 and 4). For the dependence of physical quenching rates with respect to the solvent polarity function, we found unusually high rates in benzene and methanol. This might be connected with the fact that these solvents are the ones with the lowest singlet-oxygen lifetimes in the respective polarity region investigated.

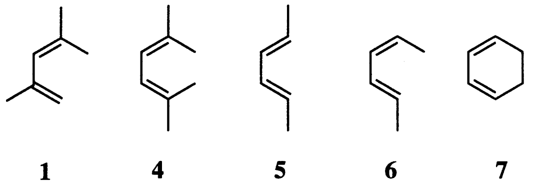
In contrast to these two reaction paths the ene reaction shows a pronounced solvent dependence. By using the Kirkwood-Laidler-Eyring model[20] we have calculated transition-state dipole moments for the [4 + 2] cycloaddition and the ene reaction of 2,5-dimethyl-2,4-hexadiene of $\mu^{\#}$ = 1.7 and $\mu^{\#}$ = 5.9 D, respectively.[11] The crucial values for the determination of these dipole moments are the slopes of the rate/polarity correlations for the photooxygenations of **1** shown in Figure 4. These values are 0.83 for the [4 + 2] cycloaddition and 4.27 for the ene reaction and thus similar to the 2,5-dimethyl-2,4-hexadiene (**4**) case (0.48 and 5.61, respectively). 1,3-cyclohexadiene (**7**) which we have used to investigate the [4 + 2] cycloaddition independently, gave a comparable value for the transition-state dipole moment $\mu^{\#} = 0.38$ D.[21] As a model compound for the ene reaction, 2-methyl-2-butene was used and a relatively low transition-state dipole moment of $\mu^{\#} = 0.92$ D was determined.[22] Obviously, the ene reaction of **1** relative to that of monoalkenes is unusually accelerated in polar solvents. Another important feature is the physical quenching of $^1O_2$ by conjugated dienes. In Table 3 the rate constants for physical and chemical quenching of $^1O_2$ by the dienes **1** and **4**–**7** (Figure 5) are summarized for CCl_4 solutions.

Table 3.

	k_o ($\times 10^5$)[a]	k_q^A ($\times 10^5$)[a]	k_{4+2} ($\times 10^5$)[a]	k_{ene} ($\times 10^5$)[a]
1	9.3	4.5	4.7	0.15
4	14.0[b]	9.6	0.22	0.25
5	1.4	0.96	0.39	–
6	0.9	0.80	0.10	–
7	32.0	–	32.0	

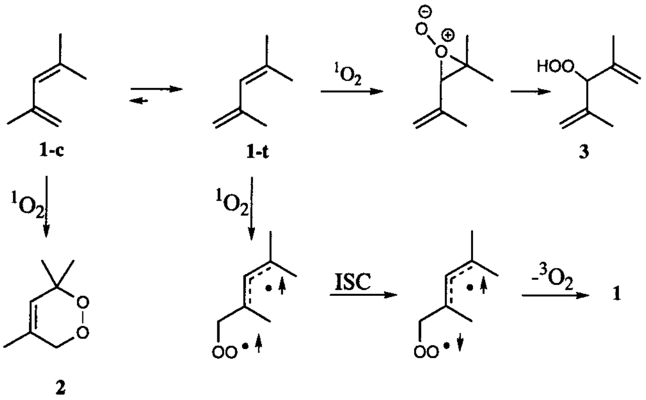
[a] In l/mol s, determined in carbon tetrachloride (TPP as sensitizer) corrected by the sensitizer quenching constant of 1.4×10^7 l/mol s ($k_o = k_q^A + k_{4+2} + k_{ene}$). – [b] k_o includes two other reaction modes: [2 + 2] cycloaddition and vinylogous ene reaction.

Figure 5. Kinetically investigated 1,3-dienes



For the highly substituted diene **4**[11] and the (*E*,*Z*)-2,4-hexadiene **6**[10] the physical quenching dominates by far the overall rate constants whereas for **1** and **5**[10] chemical and physical quenching of $^1O_2$ are of comparable magnitude. The oxygen-uptake measurements of the 1,3 cyclohexadiene (**7**) photooxygenation[21] showed no physical quenching, i.e. k_q is below ca. 0.5×10^5 M^{-1} s^{-1}. All numbers in Table 3 were determined by the oxygen-uptake method and are in accord with those published by Monroe calculated from the rubrene bleaching technique.[23] More kinetic data for singlet-oxygen [4 + 2] cycloadditions and ene reactions were collected by Wilkinson et al.[24] The results of the solvent studies for **1**, **4** and **7** (seven solvents) are consistent with a concerted mechanism for the [4 + 2] cycloaddition reaction. Aubry and co-workers have studied the [4 + 2] cycloaddition of several substituted naphthalenes in 28 solvents and reported a more pronounced solvent dependency.[25] Especially in solvents like formamide, *N*-methylformamide, trifluoroethanol and nitromethane the reaction is much more rapid than expected and an exciplex formation in these highly polar solvents was proposed. For solvents with low and medium polarity we propose the reaction mechanism depicted in Scheme 2.

Scheme 2. Proposed reaction mechanism

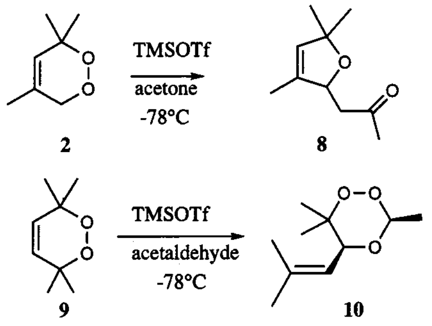


The total reactivity of the substrate can be correlated with the respective ionization potentials as shown by Monroe.[23] A concerted [4 + 2] cycloaddition requires the *cis* conformation of the substrate (**1-c**) which is in equilibrium with the *trans* conformer **1-t**. This equilibrium is shifted to the right with increasing steric repulsion, i.e. in case of the 2,5-dimethyl-2,4-hexadiene **4** the rate of [4 + 2] cycloaddition is greatly reduced. The ene reaction of **1** has a similar rate constant as for the diene **4** (Table 3). In both cases, a trisubstituted double bond is involved in the perepoxide-forming step. This interaction, however, is only about 1% of the reactivity of a trisubstituted monoalkene; e.g. for 2-methyl-2-butene a rate constant for the ene reaction in CCl_4 of 9.3×10^5 M^{-1} s^{-1} was determined.[22] The pronounced solvent dependence of the ene reaction with **1** justifies the assumption of the rate-determining formation of an perepoxide intermediate. Finally, the physical quenching of singlet oxygen by 1,3-dienes has already been reported by us to occur concomitantly with *cis-trans* isomerizations.[10] Consequently, the formation of a singlet 1,6-biradical is also postulated for substrate **1** which, after intersystem crossing to the triplet manifold, cleaves to give oxygen in the electronic ground state and the diene.

Reaction of Endoperoxide 2 with Acetone under Acid Catalysis

From compound **1** a simple monocyclic endoperoxide can be synthesized in excellent yields and purities. In order to transform this compound into a more complex 1,2,4-trioxane (in the context of recently published work on simple anti-Malaria-active peroxides[26]), we followed the TMSOTf-catalyzed addition of carbonyl compounds described by Jefford et al.[27] for bridgehead-substituted bicyclic endoperoxides. Unexpectedly, no 1,2,4-trioxane was formed when **2** was treated with TMSOTf in the presence of acetone but the tetrahydrofuran derivative **8** was detected. Thus, the TMSOTf has cleaved the peroxide O–O bond (in analogy to the acid-catalyzed Hock cleavage[28]) and the initially formed aldehyde adds one molecule of acetone to give, after dehydration, the adduct **8** (Scheme 3). A similar cleavage was observed with acetaldehyde as the carbonyl substrate.

Scheme 3. Lewis acid catalyzed rearrangement of endoperoxides **2** and **9**



That the methylene group in proximity to the peroxide linkage is responsible for this behaviour could be demonstrated by using 3,3,6,6-tetramethyldiox-4-ene (**9**), available from the photooxygenation of 2,5-dimethyl-2,4-hexadiene (**4**) in methanol[29]. After treatment with stoichiometric amounts of TMSOTf[30] in acetaldehyde at −78°C and workup, the 1,2,4-trioxane **10** was isolated in 67% yield in diastereoisomerically pure (*cis*) form. No trioxane could be isolated with acetone as the carbonyl substrate.

Conclusion

Two useful methods for the determination of singlet-oxygen reaction kinetics were compared in this report: oxygen uptake and singlet-oxygen phosphorescence measurement. The agreement between these methods was excellent. The chemical quenching of $^1O_2$ by an acceptor molecule cannot be determined easily by the phosphorescence method, and whereas the physical quenching of $^1O_2$ can be determined from the oxygen-uptake curves, the results are often erroneously. Thus, a combination of both methods allows the exact determination of both chemical and physical quenching-rate constants. The knowledge of these values is extremely important for the discussion of the reaction mechanism of photooxygenation processes.

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Experimental Section

General: All solvents (Fluka, puriss. p.a.) were redistilled from EDTA and, for chlorinated hydrocarbons also in the presence of potassium carbonate in order to exclude traces of metals and HCl. The sensitizers (Fluka) were used without further purification. The photooxygenations were performed in a 25-ml irradiation unit with a 150-W mercury high-pressure lamp in combination with a 450-nm cutoff filter. For preparative oxygenations, 0.2 M solutions of **1** were applied with ca. 3×10^{-3} M concentrations of the corresponding sensitizer.

3,3,5-Trimethyl-1,2-diox-4-ene (**2**): A solution of 480 mg (5.0 mmol) of compound **1** in 25 ml of CCl_4 (3×10^{-3} M TPP) was irradiated at 10°C under constant purging with dry oxygen until complete consumption of 4.75 mmol of oxygen. After evaporation of the solvent, the residue was distilled at 15−25°C/10^{-3} Torr which resulted in 580 mg (91%) of a colourless oil. − Molecular weight (osm.): 124 (calcd. 128). − ^{1}H NMR ($CDCl_3$, 300 MHz, 23°C): $\delta = 1.26$ (s, 6 H), 1.70 (br. s, 3 H), 4.30 (mc, 2 H), 5.49 (q, 1 H, $J = 1.6$ Hz). − ^{1}H NMR ($CDCl_3$, 300 MHz, −100°C): $\delta =$ 1.02 (s, 3 H), 1.22 (s, 3 H), 1.58 (s, 3 H), 3.94 (d, $J = 15.9$ Hz, 1 H), 4.47 (d, $J = 15.9$ Hz, 1 H), 5.41 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 17.9$ (q), 25.3 (q), 72.2 (t), 77.5 (s), 127.1 (d), 129.7 (s). − $C_7H_{12}O_2$ (318.4): calcd. C 65.59, H 9.44; found C 65.66, H 9.64.

3-Hydroperoxy-2,4-dimethylpenta-1,4-diene (**3**): A solution of 384 mg (4.0 mmol) of compound **1** in 25 ml of methanol (3×10^{-3} M RB) was irradiated at 10°C under constant purging with dry oxygen until complete consumption of 3.8 mmol of oxygen. After evaporation of the solvent, the residue was distilled at 35−42°C/10^{-1} Torr which resulted in 85 mg (16%) of a yellow oil. − ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.70$ (s, 3 H), 5.03 (br. s, 2 H), 4.69 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 18.1$ (q), 91.6 (d), 114.2 (t), 141.9 (s). − $C_7H_{12}O_2$ (318.4): calcd. C 65.59, H 9.44; found C 65.38, H 9.23.

Oxygen-Uptake Kinetics: A 25-ml irradiation unit with automatic oxygen-consumption recording system was used for analytical oxygenations. A 150-W Halogen-Bellaphot lamp (Osram) and a band filter transparent between 480 and 570 nm (Hoya) were used for electronic excitation of the sensitizers rose bengal (RB) and tetraphenylporphin (TPP). The irradiation unit and the oxygen burette were kept at 13 ± 0.1°C. The initial acceptor concentration was 3×10^{-2} M and the sensitizer concentrations between 10^{-4} M and 10^{-3} M. For determination of sensitizer quenching rates, additional TPP concentrations of 2×10^{-4} M, 4×10^{-4} M, 6×10^{-4} M, and 8×10^{-4} M were examined. As reference acceptor, 2,5-dimethylfuran (DMF) was used in initial concentrations of 2×10^{-2} M.

Phosphorescence-Quenching Experiments: About 8% (pulse energy of 3 mJ) of the total laser output of a 10-Hz Nd-YAG laser with frequency tripling to 355 nm (Continuum, Surelite-II), decoupled using a partially transmitting mirror, was used to irradiate the samples. The laser was focused (ca. 2 mm diameter) at the middle of a 1-cm quartz cuvette containing the chloroform solutions. Phosphorescence was detected at right angles to the excitation by focusing it on to the entrance slits of a 0.5-m monochromator (Acton Research) equipped with an InGaAs photodiode cooled with liquid nitrogen (Electro-Optical Systems, spectral region: 800 to 1500 nm, raise time: 3 μs).

1-(3,5,5-Trimethyl-2,5-dihydrofuran-2-yl)propan-2-one (**8**): A solution of 530 mg (4.1 mmol) of endoperoxide **2** in 10 ml of acetone was treated at −78°C with 24 μl (0.13 mmol) of trimethylsilyl trifluoromethanesulfonate (TMSOTf) under nitrogen. The mixture was stirred for 3 d at room temp. and then quenched with 40 μl of triethylamine. After evaporation of the solvent, 47.4 mg (7%) of **8** was isolated by column chromatography (Florisil 100−200 mesh; CH_2Cl_2/hexane, 1:5) as an amorphous solid. − ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.21$ (s, 6 H), 1.59 (dd, 3 H, $J = 1.1$, 1.3 Hz), 2.15 (s, 3 H), 2.45 (A-part of an ABX system, 1 H, $J = 8.3$, 14.8 Hz), 2.59 (B-part of an ABX system, 1 H, $J = 3.9$, 14.8 Hz), 4.93 (dddq, 1 H, $J = 0.8$, 1.1, 3.8, 8.3 Hz), 5.33 (dq, 1 H, $J = 0.8$, 1.3 Hz). −

^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 17.8$ (q), 17.9 (q), 28.1 (q), 31.4 (q), 49.5 (t), 83.2 (d), 86.8 (s), 130.5 (d), 135.7 (s), 207.4 (s). − MS (EI, 70 eV); *m/z* (%): 168 (12) [M$^+$], 153 (48), 111 (100), 95 (32), 83 (14), 67 (22), 55 (18).

3,6,6-Trimethyl-5-(2-methyl)propenyl-1,2,4-trioxane (**10**): A solution of 142 mg (1.0 mmol) of endoperoxide **9** in 10 ml of CH$_2$Cl$_2$ was treated at −78°C with 1 ml (29.1 mmol) of acetaldehyde and subsequently at −78°C with 200 μl (1.1 mmol) of TMSOTf under nitrogen. The mixture was stirred for 2 h at −78°C, quenched with 0.1 ml (1.4 mmol) of triethylamine, warmed up to room temp., diluted with 100 ml of CH$_2$Cl$_2$, washed with water (3 × 20 ml), and dried with MgSO$_4$. After evaporation of the solvent, 104 mg of **10** was isolated and purified by column chromatography (Florisil 100−200 mesh; CH$_2$Cl$_2$/hexane, 1:5) resulting in 71 mg (69%) of **10** as an orange oil. − ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.94$ (s, 3 H), 1.24 (d, 3 H, $J = 5.5$ Hz), 1.37 (s, 3 H), 1.69 (d, 3 H, $J = 1.4$ Hz), 1.72 (d, 3 H, $J = 1.4$ Hz), 4.23 (d, 1 H, $J = 9.2$ Hz), 5.06 (dq, 1 H, $J = 1.4, 9.2$ Hz), 5.31 (q, 1 H, $J = 5.3$ Hz). − ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 17.8$ (q), 18.6 (q), 18.7 (q), 21.9 (q), 26.1 (q), 78.9 (d), 80.6 (s), 101.3 (d), 120.2 (d), 139.3 (s). − MS (EI, 70 eV); *m/z*: 128, 110, 95, 85, 84, 83, 67, 55.

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