Photoinduced Electron-Transfer Oxidation of Olefins with Molecular Oxygen Sensitized by Tetrasubstituted Dimethoxybenzenes: A Non-Singlet-Oxygen Mechanism

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

α-Methylstyrene (**1**) was photo-oxidized in the presence of a series of alkylated dimethoxybenzenes as sensitizers in an oxygen-saturated MeCN solution to afford the cleaved ketone **2**, epoxide **3**, as well as a small amount of the ene product **4** in *ca.* 1:1:0.04 ratio. The relative rate of conversion was well-correlated with the fluorescence quantum yield of sensitizers. Thus, a non-singlet-oxygen mechanism is proposed, in which an excited sensitizer is quenched by (ground-state) molecular oxygen to produce a sensitizer radical cation and a superoxide ion ($O_2^{-\bullet}$), the former of which oxidizes the substrate, while the latter reacts with the resulting olefin radical cation ($\mathbf{1}^{+\bullet}$) to give the major oxidation products. Photodurability of such electron-donating sensitizers is dramatically improved by substituting four aromatic H-atoms in 1,4-dimethoxybenzene with Me or fused alkyl groups, which provides us with an environmentally friendly, clean method of photochemical functionalization with molecular oxygen, alternative to the ene reaction *via* singlet oxygenation.

1. Introduction. – Photosensitized oxidations with molecular oxygen (for reviews on photochemical oxidations with molecular oxygen, see [1]) have been studied extensively from the synthetic and mechanistic points of view and also as a topic of environmental significance in recent years [2]. Photoactivation of molecular oxygen with Rose Bengal (RB) and methylene blue (MB) is known to give singlet oxygen ($^1O_2$) as a key intermediate [3][4], which, in turn, reacts with olefins with allylic H-atom(s) to give the corresponding 'ene' products in good to excellent yields [3], among the various oxidation/oxygenation processes available for olefins [5].

The photoinduced singlet oxygen formation is widely accepted and successfully used in dye-sensitized oxygenations, although distinctly different mechanisms are known to operate in some specific systems. For example, singlet oxygen is almost inert to such olefins that possess no (reactive) allylic H-atom, *e.g.*, 1,1-diphenylethylene, tri- and tetraarylethylenes, and adamantylideneadamantane and derivatives. However, electron-deficient sensitizers such as dicyanoanthracene (DCA) are known to activate the photo-oxidation pathways [6]. Electron transfer from substrate to photoexcited DCA affords substrate radical cation and DCA radical anion, the latter of which reduces the ground-state oxygen to give superoxide ion ($O_2^{-\bullet}$), while the former reacts with the resulting $O_2^{-\bullet}$ to give oxidation products. It has been also suggested that, in some systems, singlet oxygen oxidizes an olefin to form radical cation/superoxide ion

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complex, leading to the formation of the dioxetane derivatives *via* a nonconcerted mechanism [7].

In establishing a practical and efficient photo-oxidation/oxygenation system, the most serious problem is the photodegradation of sensitizers. It is well-known that dye sensitizers such as RB and MB decompose upon prolonged irradiations in the presence of oxygen [8]. Cyano-aromatics, often used in electron-transfer photo-oxygenations [6], also give [2 + 2] and other cycloaddition products with olefins upon irradiation [9]. Nonconventional sensitizers, such as porphyrin derivatives [10], have been reported to give singlet oxygen *via* energy transfer, but these also suffer from degradations[2]). We have recently reported briefly that a variety of electron-donating sensitizers can be used for photo-oxidation of α-methylstyrene (**1**) with molecular oxygen[3]). In this study, we have employed a series of polyalkyl-1,4-dimethoxybenzenes as electron-donating sensitizers in order to comprehensively reveal the steric and electronic effects of the multiple alkylation of sensitizer on the photophysical properties, photochemical reactivity, chemical and quantum yields, product distribution, and photodurability of sensitizer.

Results and Discussion. – *Photolysis.* It has been reported that, in the presence of MB, α-methylstyrene (**1**) is photo-oxidized to give the corresponding ketone **2**, but no reaction details, including the reaction conditions, conversions and yields, are described in the original literature [13]. It has been proposed that MB-sensitized oxidation of (*E*)-stilbene does not proceed through the simple singlet oxygen mechanism [14] but through the electron-transfer mechanism. α-Methylstyrene is practically inert to chemically or photochemically generated singlet oxygen, but is known to be cleanly oxidized with molecular oxygen upon irradiation in the presence of 1,4-dimethoxybenzene as a sensitizer [12][15][4]).

Irradiation of an oxygen-saturated MeCN solution of **1** (2 mM) and 1,4-dimethoxybenzene (Sens = **H**, 1 mM) with a high-pressure Hg lamp (*Pyrex* filter, $\lambda > 280$ nm) at 0° gave acetophenone (**2**) and 2-methyl-2-phenyloxirane (**3**) as major products in nearly 1:1 ratio, together with a small amount of ene product **4**, as shown in *Scheme 1* and *Table 1*. The product distribution did not vary very much throughout the reaction until substrate **1** was completely consumed after 12 h irradiation. The quantum yield of conversion of **1** (Φ_{conv}) was determined as 0.15 (at low conversions of up to 10%), which was almost 10 times larger than the value obtained by direct irradiation of the olefin in the absence of sensitizer[5]). Without sensitizer, the progress of reaction was decelerated, and the relative yield of ene product **4** was increased with accompanying

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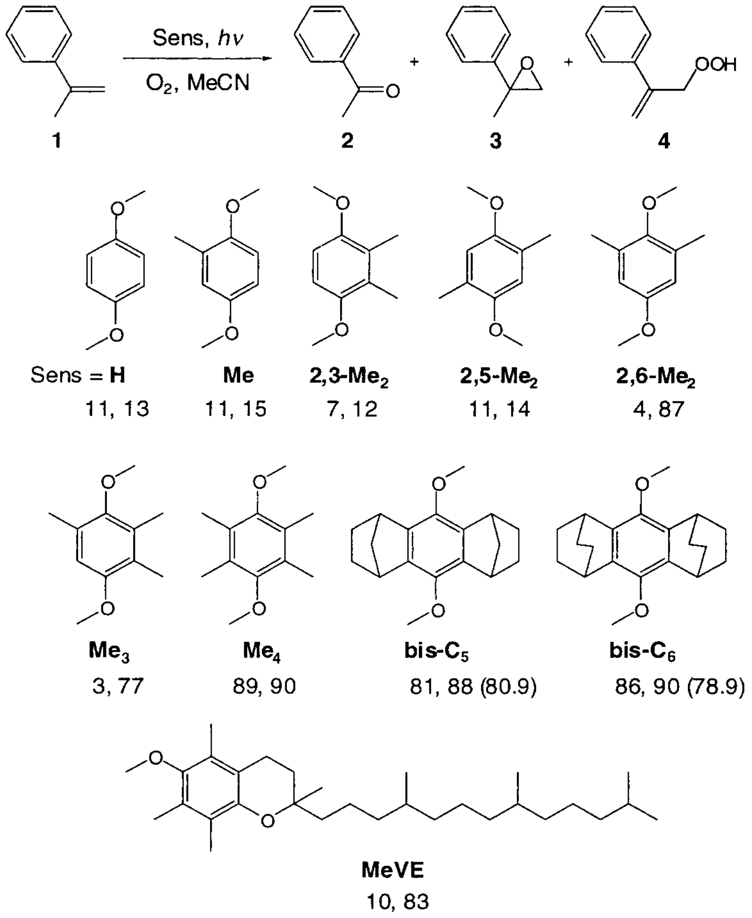
[2]) In photochemical reaction of singlet oxygen with cyclooctenes, bleaching of tetraphenylporphine as sensitizer is reported [11].

[3]) For a preliminary communication, see [12].

[4]) However, we were unable to reproduce the results reported in this report, which described a quantitative formation of acetophenone and complete recovery of the sensitizer.

[5]) Note that there is a weak tail absorption of α-methylstyrene (**1**), which allows direct excitation in the absence of sensitizer; $\varepsilon_{280} = 320\ \text{M}^{-1}\ \text{cm}^{-1}$, $\varepsilon_{290} = 110\ \text{M}^{-1}\ \text{cm}^{-1}$, and $\varepsilon_{300} = 1.6\ \text{M}^{-1}\ \text{cm}^{-1}$. However, in the presence of sensitizers, most of the incident light is absorbed by the sensitizer because of much larger absorption coefficients. After prolonged irradiation, the formation of acetophenone (**2**) retard the reaction since this also absorbs the light at $\lambda > 300$ nm. Note that the same reaction was observed even in the presence of **2**, with a lower reaction rate.

Scheme 1. *Photosensitized Oxidation of α-Methylstyrene* (**1**) *with Various 1,4-Dimethoxybenzene Derivatives.* Numbers indicate the MM2-calculated torsion angles of MeO group from the aromatic plane (in parentheses, the average angle obtained from X-ray crystallography [16]).



formation of small amount(s) of unknown by-product(s), which was not isolated by silica-gel column chromatography in sufficient quantity for further examination.

Even in the presence of sensitizer, little or no reaction occurred under Ar, clearly indicating that oxygen or air is absolutely necessary. It is also noted that the progress of reaction was extremely slow in nonpolar solvents such as hexane or methylcyclohexane. As the lifetime of singlet oxygen is known to depend only insignificantly on the solvent polarity[6]), the dramatic solvent dependence observed would indicate the non-singlet-oxygen mechanism in the present system. A previous claim that the photosensitized oxidation of **1** with 1,4-dimethoxybenzene leads to the exclusive formation of **2** at 90% conversion after 6 h of irradiation [15] was not reproducible. Instead, under analogous

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[6]) Singlet oxygen has comparable lifetimes in hexane and in MeCN ($\tau = 58$ and 31 μs, resp.) [17].

Table 1. *Photoinduced Electron-Transfer Oxidation of α-Methylstyrene* (**1**) *with Dioxygen in the Presence of Dimethoxybenzene Derivatives as Sensitizers* a)

Sens	[Sensitizer]/ mM	[**1**]/ mM	Irrad. time/h	Conversion [%]	Yield of ketone **2** [%]	Yield of oxide **3** [%]	Yield of ene product **4** [%]	Material balance [%]	Recovered sensitizer [%]	$10^2 \times \Phi_{\mathrm{conv}}$
None b)	0	2.13	1	3	3	0	0	> 95		1.9
			3	8	4	1	2	88		
			6	22	10	5	4	86		
			9	38	18	9	6	87		
			12	48	23	14	7	92		
			18	60	27	17	7	85		
			24	97	50	12	7	71		
H	1.00	2.08	1	11	2	2	< 1	36	86	15
			3	63	28	22	1	81	3	
			6	80	35	33	2	88	< 1	
			12	> 99	46	43	2	91	< 1	
Me	0.98	2.17	1	19	8	4	< 1	63	44	18
			3	74	39	32	< 1	> 95	1	
			6	98	48	40	2	92	< 1	
2,3-Me$_2$	0.97	2.22	1	36	19	12	< 1	86	18	22
			3	85	43	34	1	92	2	
			6	> 99	48	44	1	93	< 1	
2,5-Me$_2$	0.94	2.24	1	25	13	7	1	84	18	19
			3	75	36	26	2	85	7	
			6	99	51	38	3	93	3	
2,6-Me$_2$	0.91	2.07	1	5	2	1	< 1	60	80	7.3
			3	31	14	11	1	84	59	
			6	71	32	31	2	92	29	
			12	> 99	49	28	1	78	< 1	
Me$_3$	1.33	2.06	1	8	3	3	1	88	89	16
			3	70	33	26	1	86	61	
			6	96	43	43	2	92	34	
Me$_4$	0.97	2.23	1	3	1	< 1	< 1	33	> 99	4.4
			3	18	6	3	1	56	99	
			6	25	8	4	1	52	95	
			12	83	34	25	3	75	95	
			18	> 99	47	44	1	92	89	
Me$_4$ c)	0.97	2.23	12	15	2	1	< 1	20	98	–
Me$_4$ d)	0.97	2.23	12	98	94	1	< 1	> 95	98	–
bis-C$_5$	0.91	2.18	1	11	2	2	1	45	85	11
			3	47	20	14	1	74	79	
			6	72	31	25	1	79	69	
			12	> 99	41	44	1	86	71	
bis-C$_6$	0.98	2.23	1	3	1	< 1	0	33	> 99	4.6
			3	19	7	3	1	58	99	
			6	37	12	4	1	46	95	
			12	85	35	33	3	84	95	
			24	86	36	36	3	87	93	
MeVE	1.02	2.19	1	11	7	4	1	> 95	27	15
			3	61	29	18	1	79	13	
			6	89	46	30	2	88	< 1	
			12	> 99	54	30	1	85	< 1	

a) All photoreactions were carried out in oxygen-saturated MeCN solutions with a *Pyrex* filter and a high-pressure Hg lamp (*Eikosha*, 300 W, *PIH* type) at 0°, and the yields were determined by GLC analyses. b) No sensitizer added. c) DABCO (= 1,4-diazabicyclo[2.2.2]octane; 2 mM) added. d) Methanesulfonic acid (1 mM) added.

experimental conditions, we obtained **2** in less than 50% yield with a poor recovery of sensitizer **H** (*ca.* 10% recovery at 80% conversion), which is also not in agreement with the 80% recovery of 1,4-dimethoxybenzene after 12 h irradiation also reported in [15]. In this photo-oxidation as well as RB- and MB-sensitized oxygenations, photodegradation of sensitizer is frequently observed upon prolonged irradiations [8–11]. In practical synthetic applications, it is desired to develop efficient and photodurable sensitizers. To avoid unfavorable photodegradations, we successively replaced one to the four aromatic H-atoms of 1,4-dimethoxybenzene with Me or fused alkyl groups. All dimethoxybenzenes employed in this study (Sens = **H**, **Me**, **2,3-Me$_2$**, **2,5-Me$_2$**, **2,6-Me$_2$**, **Me$_3$**, **Me$_4$**, **bis-C$_5$**, **bis-C$_6$**, and **MeVE**) possess low-lying excited states (*vide infra*) and *Pyrex*-filtered light ($\lambda > 300$ nm) can be employed to effect photo-oxidation even in the presence of a substrate that absorbs light at $\lambda < 300$ nm. The results are listed in *Table 1*. Although all of the sensitizers employed gave the same oxidation products, **2**–**4**, in almost similar ratios, the relative reactivity varied dramatically.

Attempts to quench or trap the intervening singlet oxygen were unsuccessful. Although the addition of an equimolar amount of 1,4-diazabicyclo[2.2.2]octane (DABCO) as a singlet-oxygen quencher retarded the reaction by a factor of five, this is probably due to the low oxidation potential of DABCO ($E_0^{ox} = 0.64$ V *vs.* SCE) (for a singlet-oxygen quenching, see [18]). Other singlet-oxygen quenchers were not stable under the photolysis conditions. In the presence of a small amount of methanesulfonic acid, the reaction mode was completely switched to the formation of ketone **2**, which is in accordance with a recent report by *Foote et al.* [19]. Photoinduced reactions of singlet oxygen with 1-methoxy-4-[(*E*)-prop-1-enyl]benzene [19] and with $EtSCH_2Ph$ [20] can also be completely changed by adding acid. Such a dramatic modification of photoreactivity has recently been demonstrated in various photoreactions [21][22].

Spectroscopic Investigations. No appreciable ground-state interaction was observed between **1** and oxygen, affording exactly the same absorption spectra of **1** in O_2- and Ar-saturated solutions under the same conditions employed for the photolysis. Thus, the direct excitation of a charge-transfer complex in the ground-state is ruled out as the major activation pathway [23]. The singlet energies of the sensitizers were estimated from the midpoint of the (lowest-energy) absorption and fluorescence maxima (*Fig. 1*), which are listed in *Table 2*.

The electronic spectral behavior of these systematically substituted 1,4-dimethoxybenzene derivatives is interesting and indicative (see torsion angles of the MeO groups against the aromatic plane in *Scheme 1*). The successive methylation of unsubstituted sensitizer **H** up to fully substituted **Me$_4$** and **bis-C$_5$/C$_6$** leads to the significant hypsochromic shifts of the ^1L_b band of 25–30 nm. This tendency is opposite to the bathochromic shifts observed upon the relevant successive methylation of unsubstituted benzene [27]. Close examinations reveal that **Me** and **2,5-Me$_2$** do not show any significant changes in λ_{max}, while not only heavier tri- and tetrasubstitutions but also 2,6-disubstitution lead to the sudden hypsochromic shifts. These results are reasonably accounted for by assuming that the heavy substitutions hinder the *in-plane* conjugation of oxygen's lone-pair electrons with the aromatic π system. In this context, it is interesting that, although **2,5-Me$_2$** does not show any shift, the apparently analogous **2,3-Me$_2$** does give an appreciable hypsochromic shift, which would indicate that the two MeO groups should be in the *anti* conformation for better conjugation with

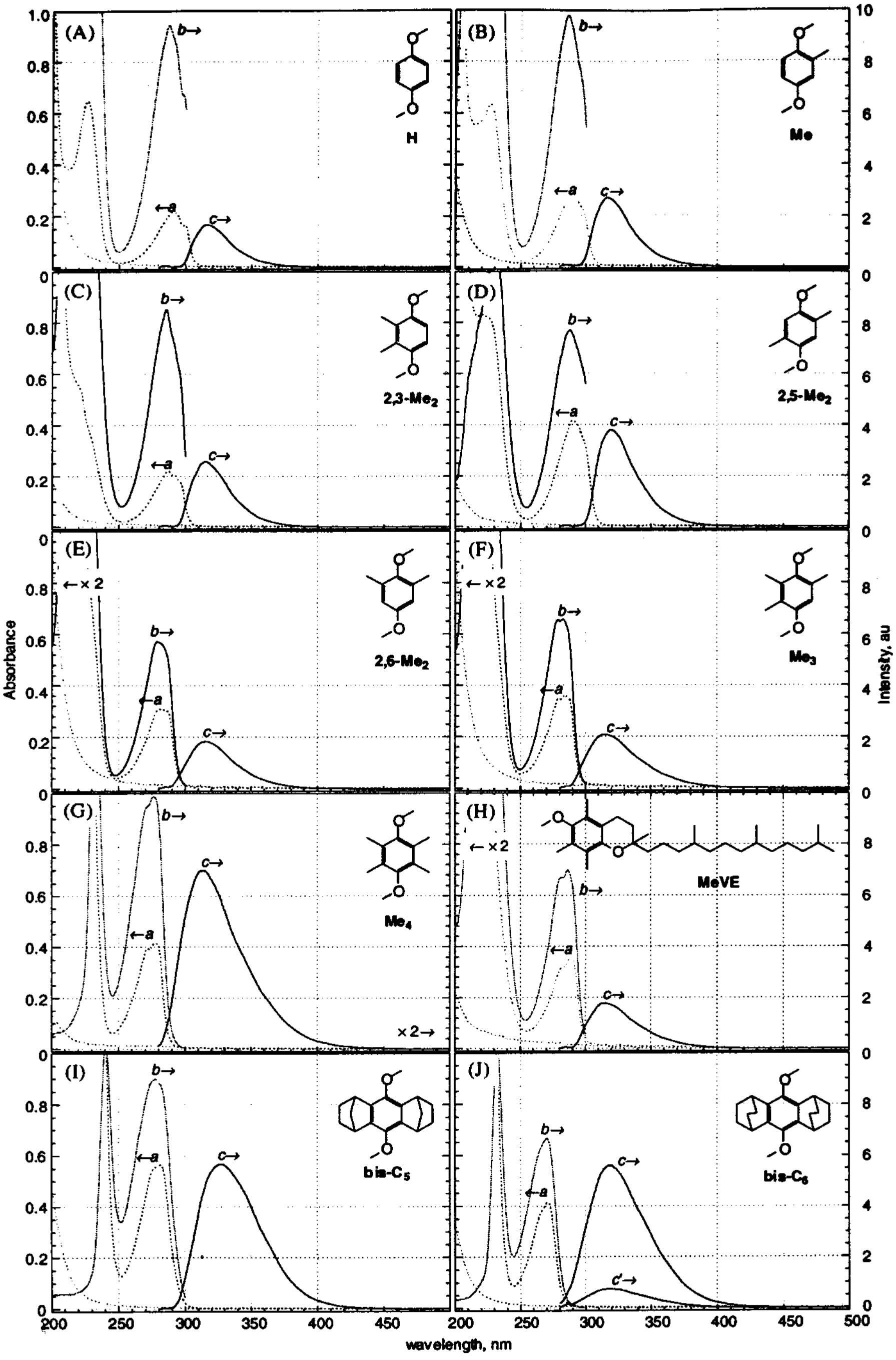

Fig. 1. *UV/VIS Absorption, fluorescence excitation, and fluorescence spectra of sensitizers in hexane solutions under comparable conditions.* See *Exper. Part* for details.

Table 2. *Photophysical Parameters of Dimethoxybenzene Derivatives (Sens)*

Sens	$\lambda(ab_1)$/ nm ^{a})	$\lambda(ab_2)$/ nm ^{a})	log ε_1	log ε_2	λ(fl)/ nm ^{a})	*Es*/ kJ mol^{-1} ^{b})	*Stokes* shift/cm^{-1}	τ_s/ns ^{c})	E_0^{ox}/V *vs.* SCE	ΔG_{ET}/ kcal mol^{-1} ^{d})	Φ_{fl} ^{e})
H	299.8	289.2	3.34	3.46	316.4	388.6	20.9	2.9 (1.04)	1.35 ^{f})	– 43.4	0.21^{2})
Me	298 ^{h})	289.0	3.42	3.52	316.2	389.9	23.1	3.0 (1.13)	1.16 ^{f})	– 48.0	0.26
2,3-Me$_2$	291.8	286.8	3.43	3.46	314.8	395.0	30.0	3.5 (1.48)	1.14 ^{f})	– 49.6	0.28
2,5-Me$_2$	299.0	290 ^{h})	3.49	3.39	319.8	387.1	26.0	3.1 (1.41)	1.02 ^{f})	– 50.5	0.30
2,6-Me$_2$	285.8	279.6	3.30	3.30	316.8	398.1	41.0	2.7 (1.16)	1.30 ^{f})	– 46.8	0.17
Me$_3$	284.0	279.2	3.36	3.35	315.4	400.3	41.9	3.2 (1.33)	1.26 ^{f})	– 48.2	0.21
Me$_4$	276.8	271.8	2.75	2.73	312.0	407.8	48.8	2.8 (1.51)	1.48 ^{f})	– 45.0	0.084
bis-C$_5$	281.2	277.8	2.79	2.78	328.0	395.1	60.7	2.0 (1.87)	1.11 ^{f})	– 50.3	0.12
bis-C$_6$	270.8	264 ^{h})	2.81	2.74	320.4	407.6	68.4	1.8 (3.44)	1.30 ^{f})	– 40.6	0.098
MeVE	289.0	282.0	3.38	3.33	315.0	396.9	34.2	3.7 (1.33)	1.05 ^{i})	– 52.1	0.22

^{a}) Absorption and fluorescence maxima obtained in hexane under Ar at 25°. ^{b}) Singlet excitation energies estimated from a midpoint of absorption and fluoroscence maxima. ^{c}) Singlet lifetime measured in hexane at 25° by a single-photon-counting method; χ^2 values in parentheses. ^{d}) The free energy change of electron-transfer process between the excited sensitizer and oxygen [24]. (b). ^{e}) Relative fluorescence quantum yields. ^{f}) From [25]. ^{g}) [26]: 0.21. ^{h}) Peak maxima were not well-separated and, therefore, estimated by the peak-fitting of double gaussian waves. ^{i}) This work.

the π system. According to MM2 calculations, the torsion angles of the two MeO groups against the benzene plane are practically the same in both **2,3-Me$_2$** and **2,5-Me$_2$**, but the two MeO groups in **2,3-Me$_2$** are *syn* to each other, while those in **2,5-Me$_2$** are *anti*. All of the sensitizers employed gave very similar splitting patterns in the ^1L_b band region (and also for the excitation spectra of each sensitizers), but the absorption coefficients (ε) varied significantly with the number of substituents on the aromatic ring. Thus, the tetrasubstituted derivatives, **Me$_4$**, **bis-C$_5$/C$_6$**, show the low ε values of several hundreds, while the less-substituted ones give much larger ε values of several thousands. Interestingly, the conformationally fixed vitamin E derivative **MeVE** as a fully substituted 1,4-dimethoxybenzene gave an exceptionally high ε value comparable with those for the less-substituted derivatives. As such, the oxidation potential of **MeVE** was measured in MeCN and compared with the relevant values of the other derivatives [25]. As can been seen from *Fig. 2*, **MeVE** exhibits good reversible redox curves upon repeated scans at a sweep rate of 100 mV s^{-1} to give the oxidation potential of $E_{1/2} = 1.05$ V (*vs.* SCE). This value is the lowest among those obtained with the sensitizers used and may be attributable to the small conformational changes upon oxidation due to the fixed conformation around the ether O-atom. α-Tocopherol and the related chromanols are known to act as antioxidants, due to such low oxidation potentials [28].

Unexpectedly, the fluorescence maxima of these sensitizers showed only slight bathochromic changes upon increasing substitution, appearing in a very narrow wavelength range of 315–325 nm. As a consequence of the hypsochromic shifts in absorption spectra, the *Stokes* shifts vary widely from 21 cm^{-1} for sensitizer **H** to 68 cm^{-1} for **bis-C$_6$**. Fluorescence quantum yields (Φ_{fl}) were measured for all sensitizers examined to give the values shown in *Table 2*; Φ_{fl} of 0.21 for 1,4-dimethoxybenzene (**H**) agrees nicely with the literature value [26]. As can be seen from *Table 2*, the Φ_{fl} values, ranging from 0.08 to 0.30, are not directly correlated with the number or pattern of aromatic substituents. Further, the fluorescence lifetimes (τ_s) of these sensitizers

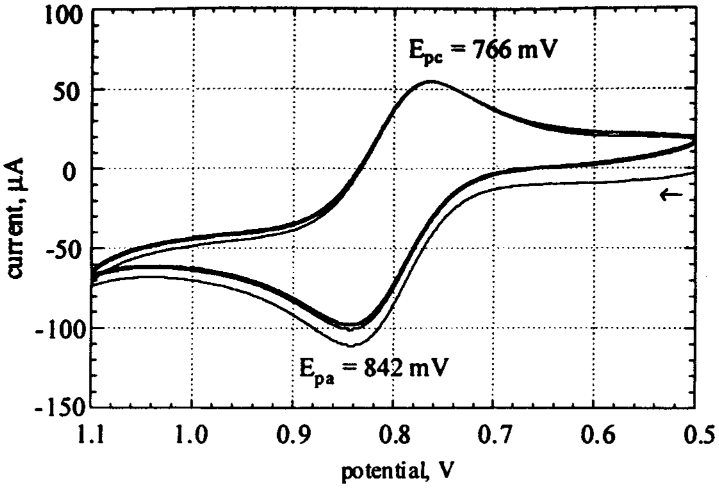

Fig. 2. *Cyclic voltammogram of 3.33 m*M **MeVE** *in MeCN containing 0.1*M *$Bu_4N^+PF_6^-$ at a sweep rate of 100 mV/ s* vs *$Ag^+/AgNO_3$. $E_{1/2}$* = 1.054 V *vs.* SCE. $E_p^a - E_p^c = 76$ mV.

were also determined as 0.77 to 3.7 ns by means of the single-photon-counting technique. Again, the tendency of τ_s is not correlated with the substitution number or pattern, but is rather in rough agreement with that of Φ_{fl}. In the lifetime analyses assuming a single exponential decay, the data for most sensitizers gave satisfactory fits with $\chi^2 \leq 1.5$, but sterically congested **bis-C$_5$** and **bis-C$_6$** showed small but appreciable deviation from the single-exponential curve, giving slightly larger χ^2 values. This would be attributed to the hindered rotation of two MeO groups in **bis-C$_5$/C$_6$**, generating two conformers possessing slightly different stabilities and lifetimes [16].

Mechanism. As can be seen from *Fig. 3*, the quantum yield of substrate consumption (Φ_{conv}) critically depends on the sensitizer employed, ranging from 0.04 to 0.22. This nicely correlates with the fluorescence quantum yield (Φ_{fl}) of each sensitizer in hexane[7]). On the contrary, no direct correlation is found between the oxidation potential (E_0^{ox}) of sensitizer and Φ_{conv}, exhibiting serious deviations particularly for sterically hindered sensitizers (*Fig. 4*). These results clearly indicate that the reaction proceeds through the singlet manifold of sensitizer. The steric bulk and the oxidation potential of alkylated sensitizers are not directly related to the product quantum yield, which is rather accounted for in terms of the population to the singlet-excited state and the process derived therefrom. Since the fluorescence and the reaction are competing processes from the singlet-excited sensitizer, one would think that, if the fluorescence efficiency is high, the reaction quantum yield should be reduced. However, in the present case, the original Φ_{fl} values obtained in hexane and particularly in MeCN are not so high (*Table 3*) and, therefore, can be used as an indicator of the relative abundance of the singlet-excited sensitizer.

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[7]) From the *Stern-Volmer*-type analysis of fluorescence, lifetimes of sensitizers in the presence of O_2, air, and Ar revealed that the quenching rates of the S1 states of sensitizers by molecular oxygen are very fast and in a range of 6–8 × 10^9, which is very close to the diffusion rate constant in MeCN at 25° (2 × 10^{10}).

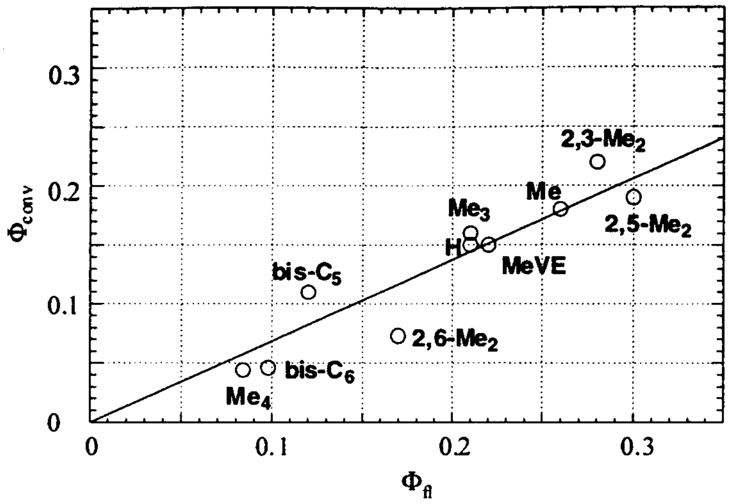


Fig. 3. *Correlation between quantum yield of fluorescence of sensitizers in hexane and relative rates of conversion* (Φ_{conv}). $\Phi_{\text{conv}} = 0.687 \times \Phi_{\text{fl}}$, $r = 0.934$.

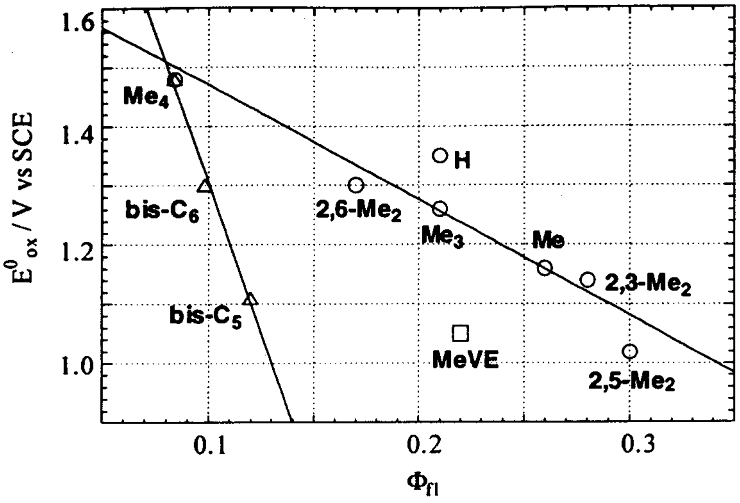


Fig. 4. *Correlation between quantum yield of fluorescence and oxidation potential of sensitizers.* $E^0_{\text{ox}} = -10.13 \times \Phi_{\text{fl}} + 2.32$, $r = 0.994$. $E^0_{\text{ox}} = -1.95 \times \Phi_{\text{fl}} + 1.67$, $r = 0.946$.

Concerning the photodurability of sensitizers (*Table 1*), we obtained good-to-excellent sensitizer recoveries of $>70\%$ even after 12 h irradiation particularly for tetrasubstituted dimethoxybenzenes **Me$_4$**, **bis-C$_5$/C$_6$**, although less-hindered ones, **Me$_3$** or **2,6-Me$_2$**, gave $\geq 50\%$ recoveries after 6 h irradiation. Phenolic compounds are known to scavenge singlet oxygen in biological systems through the 1,4-cycloaddition to electron-rich aromatic ring systems to produce endoperoxides [30]. Accordingly,

Table 3. *Photophysical Parameters of Durohydroquinone Dimethylether* (**Me$_4$**) *in Various Solvents*

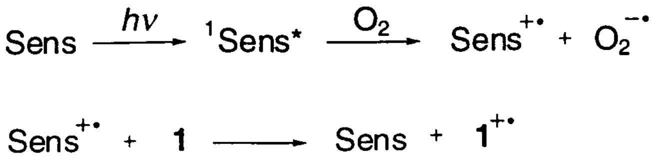
Solvent	E_T(30)/kcal mol^{-1} [a])	ε [b])	λ(ab$_1$)/nm [c])	λ(ab$_2$)/nm [c])	ε_{277}/M^{-1} cm^{-1}	ε_{272}/M^{-1} cm^{-1}	λ(fl)/nm [c])	τ_s/ns [d])	Φ_{fl} [e])
MeOH	55.5	35.9	276.2	271.2	468	454	314.4	1.4	0.037
MeCN	46.0	32.7	276.6	271.4	461	441	314.8	1.9	0.047
CH_2Cl_2	41.1	8.93	277.0	272.0	514	490	315.4	0.7	0.018
Et_2O	34.6	4.34	277.0	271.6	564	529	313.2	2.5	0.080
C_6H_{14}	30.9	1.89	276.8	271.8	563	531	312.0	2.8	0.084

[a]) Empirical solvent polarity [29]. [b]) Dielectric constant [26]. [c]) Absorption and fluorescence maxima obtained in hexane under Ar at 25°. [d]) Singlet lifetime measured at 25° by a single-photon-counting method. [e]) Relative fluorescence quantum yields.

similar oxygenation of the sensitizers may account at least in part for the degradation pathways [5][10b].

We propose the electron-transfer oxidation mechanism illustrated in *Schemes 2* and *3* for the present system, since we observed the strong solvent dependence and the good correlation between Φ_{fl} and Φ_{conv}, which are not compatible with the singlet-oxygen mechanism. The free energy change of electron transfer from the excited sensitizer to oxygen can be evaluated by the *Rehm-Weller* equation [24]: ΔG_{ET} (in kcal mol^{-1}) = $23.06 \times [E(\mathrm{Sens/Sens}^{+\bullet}) - E(O_2^{-\bullet}/O_2) - e_0^2/a\varepsilon - \Delta E_{0,0}]$, where $E(O_2^{-\bullet}/O_2) = -0.86$ V *vs.* SCE [31] and $e_0^2/a\varepsilon = 0.06$ V [24]. Highly favorable free energy changes of $\Delta G_{ET} < -40$ kcal mol^{-1} were obtained for all of the sensitizers employed in this study.

Scheme 2



As illustrated in *Scheme 2*, the singlet-excited sensitizer reduces molecular oxygen to generate a sensitizer radical cation and superoxide ($O_2^{-\bullet}$), the former of which oxidizes substrate **1** to give the radical cation **1**$^{+\bullet}$, which in turn reacts with superoxide to form the perepoxide intermediate **5** (*Scheme 3*) [32]. The perepoxide thus produced affords the corresponding epoxide **3** either through the reaction with singlet oxygen[8]) or through the reaction with another molecule of **5** [34].

Dioxetane intermediates are often isolated in the photo-oxygenation of sterically hindered olefins such as adamantylideneadamantane and its derivatives [35][36]. Hence, it is reasonable to assume that dioxetane **7** is formed as an intermediate in the present system but cannot survive under the reaction conditions employed [37], ultimately affording acetophenone (**2**) and formaldehyde (**8**) as the final products. *Barton*-type oxidation [36], *i.e.*, the addition of triplet (ground-state) oxygen to the

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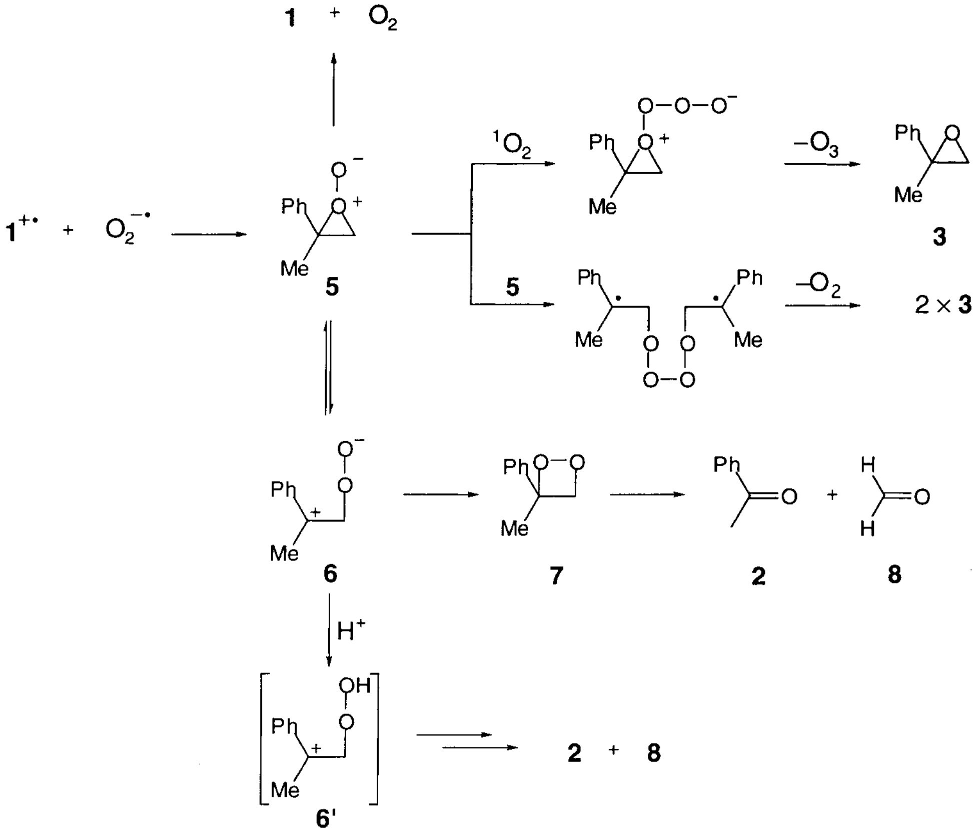
[8]) Judging from the relatively high quantum yields (*ca.* 0.5) of intersystem crossing for methoxybenzenes, singlet oxygen should be formed in the present system through the energy transfer from the triplet sensitizers to oxygen. Photolysis product **2** can also act as a triplet sensitizer for generation of singlet oxygen. For addition of singlet oxygen to the perepoxide and the subsequent cleavage releasing ozone, see [33].

Scheme 3



substrate radical cation $1^{+\bullet}$, leading to the chain oxidation process, may not be operative as the major pathway, because the quantum yields obtained are much lower than unity in the present cases. In the presence of acid, adduct **6** is trapped to form the protonated cationic species **6′**, which eventually produces acetophenone (**2**) in excellent yield [18] without giving epoxide **3** (*Scheme 3*).

Conclusion. – By using (tetrasubstituted) dimethoxybenzenes as sensitizers, we achieved an efficient photosensitized oxidation of olefins with molecular oxygen to afford the corresponding ketone and epoxide, as well as a small amount of ene product in excellent combined yields. This reaction does not appear to involve the singlet-oxygen mechanism, as judged from the strong solvent effect and the good correlation between the fluorescence quantum yield of sensitizer and the relative rate of conversion. The proposed oxidation mechanism involves the initial quenching of singlet-excited sensitizer by molecular oxygen to produce sensitizer radical cation and superoxide, which is followed by the electron transfer from the substrate olefins to the sensitizer radical cation and the subsequent recombination of the resulting substrate radical cation with the superoxide, producing the ketone and epoxide as the major oxidation products (*Schemes 2* and *3*).

Finally, it is noted that the photodurability of 1,4-dimethoxybenzene sensitizers is a critical function of the nuclear substitution and dramatically enhanced by heavy alkylation. The very high photodurability of tetraalkyl-1,4-dimethoxybenzene sensitizers provides us with a promising new methodology for clean photo-oxidation processes, which are essentially environmentally friendly.

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Experimental Part

General. α-Methylstyrene (*Wako*), Zn powder (*Wako*), MeI (*Kanto*), NaH in oil (*Wako*), AcOH (*Wako*), THF (*Wako*), benzophenone (*Wako*), Na (*Wako*), methylbenzoquinone (*Aldrich*), 2,3-dimethylbenzoquinone (*Aldrich*), 2,5-dimethylbenzoquinone (*Acros*), 2,6-dimethylbenzoquinone (*TCI*), trimethylbenzoquinone (*Aldrich*), duroquinone (*Acros*), α-DL-tocopherol (*Aldrich*), 1,4-benzoquinone (*Aldrich*), cyclohexa-1,3-diene (*Acros*), dicyclopentadiene (*Wako*), 10% Pd/C (*Wako*), Br (*Junsei*) were commercially available and used as received. All solvents were purified as described in the literature [37]. MeCN (*Kanto*) was refluxed with $KMnO_4$ and $LiCO_3$ for 1 h, decanted, and fractionally distilled from CaH_2 and stored in a *Schlenk*-type container under Ar in the dark. Hexane (*Wako*) was also shaken with conc. H_2SO_4 until the acid layer turned no longer yellow, washed with H_2O and aq. $NaHCO_3$, and purified by fractional distillation. EtOH (*Wako*) was distilled from CaH_2 before use and stored over molecular sieves (4 Å) under Ar. Cyclododecane (*TCI*) used as an internal standard for GLC analyses was recrystallized from EtOH. All the (photolysis) products were purified either by recrystallization from EtOH, by silica-gel column chromatography with hexane/AcOEt (50 : 1 → 1 : 1), or by GPC column chromatography (*Jaigel 1-H* and *2-H* from *Japan Analytical Industry Co.*) with $CHCl_3$ and identified from the comparison with authentic samples. The ene product **4** was identified as a corresponding alcohol (α-methyl-β-hydroxystyrene = 2-methyl-2-phenylprop-1-en-1-ol) obtained upon reaction with Me_3P.

Instruments. GC Analyses of photolyzed samples were run on a *Shimadzu GC-14B* instrument fitted with a *C-R6A* integrator and a cap. column (*SGE*, *BPX5*, 30 m × 0.22 mm i.d.). ^1H- and ^{13}C-NMR spectra were obtained on a *JEOL GX-400* instrument in $CDCl_3$ with Me_4Si (for ^1H) or $CHCl_3$ (for ^{13}C, appearing at 77.16 ppm) as an internal standard. GC/MS analyses (EI) were performed on *Hewlett-Packard HP5890* Series *II* and *HP5971A* mass-selective detector with an acceleration voltage of 70 eV. Elemental analysis was performed in the Center for Chemical Analyses, Osaka University. Fluorescence-lifetime measurements were run with an Ar-sat. soln. of sensitizers (*ca.* 0.1 mM) on *Horiba NAES-550* fitted with *SCN-121A* (optical chamber), *NFL-111A* (pulsed H_2 light source), *SGM-121A* (monochromator), *SSU-111A* (photomultiplier), *LPS-111* (lamp power supply), and *Advantec LCH-111 Labo Thermo-Cool* temp. controller. The radiation from the lamp was made monochromatic by 10-nm monochromator (centered at 260 nm), and the emission from the sample solution was detected through a *Toshiba UV31* or *UV33* filter.

Steady-State Electronic Absorption and Fluorescence Spectral Measurements. Absorption spectra were recorded on a *JASCO V-550* spectrometer with an *ETC-505T* temp. controller, and fluorescence spectra were recorded on *JASCO FP-777* for Ar-saturated solns. For emission spectra, the excitation wavelength was fixed at 260 nm, and both of the excitation and emission slit widths were 3 nm throughout the study. For fluorescence excitation spectra, detailed conditions for each sample corresponding to *Fig. 1* are as follows: *A*) *a:* UV, 0.0724 mM; *b:* excitation, 0.0724 mM, $\lambda_{em} = 320$ nm; *c:* emission, 0.0724 mM. *B*) *a:* UV, 0.0815 mM; *b:* excitation, 0.0815 mM, $\lambda_{em} = 330$ nm; *c:* emission, 0.0815 mM. *C*) *a:* UV, 0.0740 mM; *b:* excitation: 0.0740 mM, $\lambda_{em} = 330$ nm; *c:* emission: 0.0740 mM. *D*) *a:* UV, 0.1059 mM; *b:* excitation: 0.1059 mM, $\lambda_{em} = 340$ nm; *c:* emission, 0.1059 mM. *E*) *a:* UV, 0.0728 mM; *b:* excitation, 0.0728 mM, $\lambda_{em} = 330$ nm; emission, 0.0728 mM. *F*) *a:* UV, 0.0749 mM; *b:* excitation, 0.0749 mM, $\lambda_{em} = 320$ nm; *c:* emission, 0.0749 mM. *G*) *a*, UV: 0.715 mM; *b:* excitation, 0.715 mM, $\lambda_{em} = 320$ nm; *c:* emission, 0.715 mM. *H*) *a:* UV: 0.0699 mM; *b:* excitation, 0.0699 mM, $\lambda_{em} = 320$ nm; *c:* emission, 0.0699 mM. *I*) *a:* UV: 0.910 mM; *b:* excitation, 0.910 mM, $\lambda_{em} = 320$ nm; *c:* emission: 0.910 mM. *J*) *a:* UV, 0.633 mM; *b:* excitation, 0.633 mM, $\lambda_{em} = 320$ nm; *c:* emission, 0.0633 mM; *c′:* emission: 0.633 mM.

Measurement of Oxidation Potential of Methylated α-DL-Tocopherol. Cyclic voltammetry was performed on a *BAS CV-100B* electrochemical analyzer. Substrate **MeVE** (3.33 mM) and electrolyte were placed in a gas-tight *Schlenk*-type separated cell under Ar. Anodic and cathodic peak potentials were measured with a Pt electrode in MeCN containing 0.1M $Bu_4N^+PF_6^-$ at a sweep rate of 100 mV s^{-1}. The $Ag^+/AgNO_3$ reference electrode was used and calibrated with ferrocene ($E_{1/2} = 20$ mV), and the measured potential was converted to the voltage *vs.* SCE by means of the relationship: $E(\mathrm{SCE}) = E(\mathrm{Ag^+/AgNO_3}) + 0.25$ V.

Photolysis. A typical procedure for the photo-oxidation of α-methylstyrene (**1**) is as follows: **1** (6.24 mg, 2.11 mM), dimethoxybenzene sensitizer (Sens, 1 mM), and cyclododecane (1 mg) were dissolved in dry MeCN in a 25-ml volumetric flask. After sonication, 3-ml portions of the soln. were distributed to *Pyrex* tubes (outside diameter of 10 mm). The mixture was cooled to 0° and bubbled with O_2 gas for 3 min. Each tube was sealed with a rubber septum, placed in a MeOH bath at 0°, and temp.-controlled by a combination of *Neslab CC-100* and *Koike TC-01* thermocontroller. Irradiations were conducted, with a 300-W high-pressure Hg lamp (*Eikosha*, *PIH* type, $\lambda > 280$ nm). The sample tubes were directly attached to the lamp surface through the cooling jacket at a distance of *ca.* 1 mm. After a given period of irradiation, the photolysis was quenched with H_2O and the soln. was extracted with CH_2Cl_2, and the org. phase was directly submitted to GLC.

Quantum-Yield Measurement. Quantum efficiency of conversion (Φ_{conv}) was determined at low conversion stages ($\leq 10\%$) by using the photoisomerization reaction of 4-methylbenzonitrile in MeCN at 25° under Ar as a chemical actinometer [39]. Relative fluorescence quantum yields (Φ_{fl}) were determined in Ar-sat. hexane soln. at 22° in order to estimate the relative abundance of the singlet excited species in solution by the standard method with quinine sulfate in 1N H_2SO_4 as reference ($\Phi_{\mathrm{fl}} = 0.546$) [40].

Synthesis of Sensitizers. Methylated α-DL-tocopherol **MeVE** was synthesized by direct methylation of α-tocopherol. α-DL-Tocopherol (17.1 g, 40 mmol) was dissolved in THF (100 ml), to which NaH in oil (*ca.* 60%, 1.8 g, *ca.* 45 mmol) was added in one portion at an ice-cool temp. under Ar. The soln. was stirred for 1 h and MeI (2.7 ml, 44 mmol) was added all at once, and then the soln. was refluxed for 15 h. The resulting soln. was poured into H_2O, and the mixture was extracted with Et_2O (2×50 ml). The Et_2O extract was washed with H_2O (2×50 ml) and dried (Na_2SO_4). After filtration and evaporation, the crude material obtained was chromatographed (silica gel; hexane/AcOEt 50:1) to afford yellowish solid. This material was further purified by recrystallization from $EtOH/CH_2Cl_2$. Yield 16.1 g (91%). White solid. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 (*d*, $J = 6.5$, 3 H); 0.88 (*d*, $J = 6.5$, 3 H); 0.89 (*d*, $J = 6.5$, 6 H); 1.02 – 1.64 (*m*, 21 H); 1.26 (*s*, 3 H); 1.81 (sym. *m*, $J = 6.9$, 2 H); 2.11 (*s*, 3 H); 2.16, (*s*, 3 H); 3.65 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 11.82; 11.90; 12.69; 19.82; 19.90; 20.79; 21.18; 22.78; 22.87; 24.04; 24.60; 24.96; 28.13; 31.44; 32.86; 32.96; 37.44; 37.57; 37.61; 37.63; 39.53; 40.21; 60.52; 74.91; 117.66; 123.03; 125.83; 127.86; 147.91; 149.52. EI-MS (70 eV): 445 (39, $[M+1]^+$), 444 (100, M^+), 430 (7), 180 (5), 179 (36), 178 (7). Anal. calc. for $C_{30}H_{52}O_2$: C 81.02, H 11.79, found: C 80.86, H 11.67.

Fused sensitizers **bis-C$_5$** and **bis-C$_6$** were obtained according to the literature procedures [16]. All of the other methylated sensitizers were synthesized according to the conventional procedures, *i.e.*, dimethylation of the corresponding hydroquinone with MeI/NaH in THF at 25°. The hydroquinones are either commercially available or obtained from the reduction of the corresponding benzoquinones with Zn in AcOH [25]. All of the methylated hydroquinone dimethyl ethers used in this study have been already reported in the literature. Hence, only the EI-MS data are summarized below: *1,4-dimethoxy-2-methylbenzene* (**Me**): 153 (9, $[M+1]^+$)), 152 (82, M^+), 138 (9), 137 (100), 109 (15), *1,4-dimethoxy-2,3-dimethylbenzene* (**2,3-Me$_2$**): 167 (11, $[M+1]^+$), 166 (85, M^+), 152 (13), 151 (100), 121 (21), 91 (14); *1,4-dimethoxy-2,5-dimethylbenzene* (**2,5-Me$_2$**): 167 (9, $[M+1]^+$), 166 (79, M^+), 152 (11), 151 (100), 123 (13); *1,2-dimethoxy-2,6-dimethylbenzene* (**2,6-Me$_2$**) : 167 (9, $[M+1]^+$), 166 (70, M^+), 152 (13), 151 (100), 123 (18), 91 (11); *1,4-dimethoxy-2,3,6-trimethylbenzene* (**Me$_3$**): 181 (9 $[M+1]^+$), 180 (66, M^+), 166 (13), 165 (100), 137 (16); *1,4-dimethoxy-2,3,5,6-tetramethylbenzene* (**Me$_4$**): 195 (11, $[M+1]^+$), 194 (72, M^+), 180 (15), 179 (100), 154 (14), 136 (16); *9,10-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene* (**bis-C$_5$**): 271 (15 $[M+1]^+$), 270 (69, M^+), 243 (20), 242 (100), 214 (57), 199 (28), 107 (13); *9,10-dimethoxy-1,4:5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene* (**bis-C$_6$**): 299 (25 $[M+1]^+$), 298 (100, M^+), 283 (11), 270 (34), 269 (23), 255 (20), 201 (11).

REFERENCES

[1] a) S. Vasenkov, H. Frei, *Mol. Supramol. Photochem.* **2000**, *5*, 295; b) C. Tanielian, R. Mechin, R. Seghrouchni, C. Schweitzer, *Photochem. Photobiol.* **2000**, *71*, 12; c) N. Satoh, S. Fukuzumi, *Rev. Heteroat. Chem.* **1999**, *20*, 249; d) T. Tanaka, H. Yoshida, *Hyomen Kagaku* **1999**, *20*, 73; e) H. Frei, *Brookhaven Natl. Lab., [Rep.] BNL* **1995**, *61733*, 18; f) T. Akasaka, W. Ando, *Yuki Gosei Kagaku Kyokaishi* **1993**, *51*, 212;

g) L. Lopez, *Top. Cur. Chem.* **1990**, *156*, 117; h) M. A. Fox, in 'Photoinduced Electron Transfer, Vol. Pt. D,' Ed. M. A. Fox, M. Chanon, Elsevier, Amsterdam, Netherlands, 1988, pp. 1; i) K. H. Pfoertner, *Spec. Publ. – R. Soc. Chem.* **1986**, *57*, 189; j) C. S. Foote, *Tetrahedron* **1985**, *41*, 2221; k) J. F. Rabek, *Wiad. Chem.* **1971**, *25*, 435.

[2] a) B. Ranby, J. F. Rabek, 'Photodegradation, Photooxidation and Photostabilization of Polymers', Wiley, London, 1975; b) M. S. A. Abdou, S. Holdcroft, *Macromolecules* **1993**, *26*, 2954; c) R. D. Scurlock, B. Wang, P. R. Ogilby, R. L. Clough, *J. Am. Chem. Soc.* **1995**, *117*, 10194; d) M. J. Thomas, C. S. Foote, *Photochem. Photobiol.* **1978**, *27*, 687; e) R. W. Denny, A. Nickon, *Org. React.* **1973**, *20*, 133.

[3] M. Stratakis, M. Orfanopoulos, *Tetrahedron* **2000**, *56*, 1595.

[4] a) C. S. Foote, *Acc. Chem. Res.* **1968**, *1*, 104; b) L. M. Stephenson, M. J. Grdina, M. Orfanopoulos, *Acc. Chem. Res.* **1980**, *13*, 419; c) C. S. Foote, E. L. Clennan, in 'Active Oxygen in Chemistry,' Ed. C. S. Foote, J. S. Valentine, A. Greenberg, J. F. Liebman, Chapman & Hall, London, 1995, p 105; d) A. A. Frimmer, L. M. Stephanson, in 'Singlet Oxygen. Reactions, Modes and Products,' Ed. A. A. Frimer, CRC Press, Boca Raton, FL, 1985; e) H. H. Wasserman, J. L. Ives, *Tetrahedron* **1981**, *37*, 1825; f) H. H. Wasserman, R. W. Murray, in 'Singlet Oxygen,' Academic Press, New York, 1979.

[5] E. A. Lissi, M. V. Encinas, E. Lemp, M. A. Rubio, *Chem. Rev.* **1993**, *93*, 699.

[6] a) J. Eriksen, C. S. Foote, T. L. Parker, *J. Am. Chem. Soc.* **1977**, *99*, 6455; b) K. A. Zaklika, B. Kaskar, A. P. Schaap, *J. Am. Chem. Soc.* **1980**, *102*, 386; c) A. P. Schaap, K. A. Zaklika, B. Kaskar, W.-M. Fung, *J. Am. Chem. Soc.* **1980**, *102*, 389; d) L. T. Spada, C. S. Foote, *J. Am. Chem. Soc.* **1980**, *102*, 391.

[7] a) C. S. Foote, J. W. P. Liu, *Tetrahedron Lett.* **1968**, 326; b) C. S. Foote, A. A. Dzakapasu, J. W. P. Liu, *Tetrahedron Lett.* **1975**, 1247.

[8] a) T. J. Dougherty, *Photochem. Photobiol.* **1987**, *45*, 879; b) J. J. McCullough, *Chem. Rev.* **1987**, *87*, 811.

[9] a) T. Kubo, T. Inoue, H. Sakai, *J. Am. Chem. Soc.* **1992**, *114*, 7660; b) H. J. P. de Lijser, D. R. Arnold, *J. Org. Chem.* **1997**, *62*, 8432; c) K. Mizuno, R. Kaji, Y. Otsuji, *Chem. Lett.* **1977**, 1027; d) N. C. Yang, D. M. Shold, J. K. McVey, *J. Am. Chem. Soc.* **1975**, *97*, 5004; e) N. C. Yang, K. Srinivasachar, B. Kim, J. Libman, *J. Am. Chem. Soc.* **1975**, *97*, 5006.

[10] a) C. Tanielian, C. Wolff, *J. Phys. Chem.* **1995**, *99*, 9825; b) D. Murtinho, M. Pineiro, M. M. Pereira, A. M. d'A. R. Gonsalves, L. G. Arnaut, M. da Graa Miguel, H. D. Burrows, *J. Chem. Soc., Perkin Trans. 2* **2000**, 2441.

[11] T. H. W. Poon, K. Pringle, C. S. Foote, *J. Am. Chem. Soc.* **1995**, *117*, 7611.

[12] T. Mori, M. Takamoto, Y. Tate, J. Shinkuma, T. Wada, Y. Inoue, *Tetrahedron Lett.* **2001**, *42*, 2505.

[13] D. R. Kearns, W. Fenical, P. Radlick, *Ann. N. Y. Acad. Sci.* **1970**, *171*, 34.

[14] L. E. Manring, J. Eriksen, C. S. Foote, *J. Am. Chem. Soc.* **1980**, *102*, 4275.

[15] U. T. Bhalerao, M. Sridhar, *Tetrahedron Lett.* **1993**, *34*, 4341.

[16] R. Rathore, J. K. Kochi, *J. Org. Chem.* **1994**, *60*, 4399.

[17] M. A. J. Rodgers, *J. Am. Chem. Soc.* **1983**, *105*, 6201.

[18] C. S. Foote, in 'Singlet Oxygen', Academic Press, New York, 1979, p. 139; b) C. Ovannés, T. Wilson, *J. Am. Chem. Soc.* **1968**, *90*, 6528; c) H. Görner, D. Schulte-Frohlinde, *Chem. Phys. Lett*. **1986**, *124*, 321.

[19] A. Greer, G. Vassilikogiannakis, K.-C. Lee, T. S. Koffas, K. Nahm, C. S. Foote, *J. Org. Chem.* **2000**, *65*, 6876.

[20] S. M. Bonesi, M. Mella, N. d'Alessandro, G. G. Aloisi, M. Vanossi, A. Albini, *J. Org. Chem.* **1998**, *63*, 9946.

[21] T. Mori, T. Wada, Y. Inoue, *Org. Lett.* **2000**, *2*, 3401.

[22] a) N. Hoffmann, J.-P. Pete, *J. Org. Chem.* **1997**, *62*, 6952; b) N. Hoffmann, J.-P. Pete, *Tetrahedron Lett.* **1998**, *39*, 5027; c) J.-H. Ho, T.-I. Ho, R. S. H. Liu, *Org. Lett.* **2001**, *3*, 409.

[23] a) S. Hashimoto, H. Akimoto, *J. Phys. Chem.* **1987**, *91*, 1347; b) F. Blatter, F. Moreau, H. Frei, *J. Phys. Chem.* **1994**, *98*, 13403; c) H. Sun, F. Blatter, H. Frei, *ACS Symp. Ser.* **1996**, *638*, 409; d) T. Kodaira, K. Hayashi, T. Ohnishi, *Polym. J.* **1973**, *4*, 1; e) D. G. M. Wood, T. M. Kollmau, *Chem. Ind.* **1972**, 423.

[24] a) D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, *8*, 259; b) D. Rehm, A. Weller, *Z. Phys. Chem.* **1970**, *69*, 183.

[25] R. Rathore, E. Bosch, J. K. Kochi, *Tetrahedron* **1994**, *50*, 6727.

[26] 'Handbook of Photochemistry', 2nd edn., Ed. S. L. Murov, I. Carmichael, G. L. Hug, Marcel Dekker, Inc., New York, 1993.

[27] 'DMS UV Atlas of Organic Compounds', Ed. H.-H. Perkampus, I. Sandeman, C. J. Timons, Verlag Chemie, Weinheim, Butterworths, London, 1966–71.

[28] a) D. P. R. Muller, M. A. Goss-Sampson, *Crit. Rev. Neurobiol.* **1990**, *5*, 239; b) G. W. Burton, A. Joyce, K. U. Ingold, *Arch. Biochem. Biophys.* **1983**, *221*, 281; c) M. T. Craw, M. C. Depew, *Rev. Chem. Intermed.* **1985**, *6*, 1; d) S. Sur, J. P. Colpa, *Chem. Phys. Lett.* **1986**, *127*, 577.

[29] C. Reichardt, *Angew. Chem., Int. Ed.* **1979**, *18*, 78.

[30] a) A. L. Tappel, *Vitam. Horm. (N. Y.)* **1962**, *20*, 493; b) P. P. Nair, R. N. Patnaik, J. W. Hauswirth, in 'Tocopherol, Oxygen and Biomembranes', Ed. C. Deduve, O. Hayashi, Elsevier Press, New York, 1978, 121; c) K. A. Fukuzawa, A. Tokumura, S. Ouchi, H. Tsukatani, *Lipids* **1982**, 511.
[31] C. Shi, F. C. Anson, *J. Electroanal. Chem.* **2000**, *484*, 144.
[32] a) T. Kanno, T. Oguchi, H. Sakaragi, K. Takamoku, *Tetrahedron Lett.* **1980**, *21*, 467; b) M. A. Fox, C. C. Chen, *J. Am. Chem. Soc.* **1981**, *103*, 6757; c) M. A. Fox, J. N. Younathan, *Tetrahedron* **1986**, *42*, 6285; d) Y. Taniguhi, A. Mioshi, N. Mataga, H. Shizuka, T. Morita, *Chem. Phys. Lett.* **1972**, *15*, 2223.
[33] P. D. Bartlett, *Chem. Soc. Rev.* **1976**, 149.
[34] J. Eriksen, C. S. Foote, *J. Am. Chem. Soc.* **1980**, *102*, 6083.
[35] a) C. W. Jefford, A. F. Boschung, *Helv. Chim. Acta* **1977**, *60*, 2673; b) A. P. Schaap, G. R. Faler, *J. Am. Chem. Soc.* **1973**, *95*, 3381.
[36] a) D. H. R. Barton, G. Leclerc, P. D. Magnus, I. D. Menzics, *J. Chem. Soc., Chem. Commun.* **1972**, 447; b) S. F. Nelsen, R. Akaba, *J. Am. Chem. Soc.* **1981**, *103*, 2096; c) S. F. Nelsen, D. L. Kapp, R. Akaba, D. H. Evans, *J. Am. Chem. Soc.* **1986**, *108*, 6863.
[37] W. H. Richardson, F. C. Montgomery, M. B. Yelvington, H. E. O'Neal, *J. Am. Chem. Soc.* **1974**, *96*, 7525.
[38] 'Purification of Laboratory Chemicals', 4th edn., Ed. W. L. F. Ararego, D. D. Perrin, Reed Educational and Professional Publishing Ltd, Oxford, 1996.
[39] R. J. MacLeod, A. L. Pincock, J. A. Pincock, K. A. Thompson, *J. Am. Chem. Soc.* **1998**, *120*, 6443.
[40] J. N. Demas, G. A. Crosby, *J. Phys. Chem*. **1971**, *75*, 991.

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