(λ = 0.71069). Only random fluctuations of less than 2% in the intensities of two standard reflections were observed during the course of data collection. The structure of *N*-(1-phenylethyl)-methanesulfinamide was solved by direct methods and an absorption correction was applied. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. The largest feature on a final difference map was 0.31 e Å^{-3} in height. The largest shift in the final cycle of refinement was 0.030 for overall scale. A summary of the relative experimental parameters for the X-ray structure determination of the sulfinamide, atomic coordinates, isotropic thermal parameters, a listing of the bond distances and bond angles as well as hydrogen-atom coordinates are given as supplementary materials. A computer projection of the structure is reproduced in Figure 1.

The relative experimental parameters for the X-ray structure determination of 3-((1-phenylethyl)ammonio)propanesulfinate are summarized in the supplementary material. No decay in the intensities of two standard reflections was observed during the course of data collection. The structure was solved by direct methods, and an absorption correction was applied. The handedness was determined to be correct as found by use of the SHELXTL routine for this purpose. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bonded to carbon were included at calculated positions using a riding model, with C–H of 0.96 Å and $U_H = 1.2U_C$. The largest feature on a final difference map was 0.65 e Å^{-3} in height in the approximate position of the sulfur lone pair. The largest shift in the final cycle of refinement was 0.013. Atomic coordinates, isotropic thermal parameters, a listing of the bond distances and bond angles as well as hydrogen-atom coordinates are given as supplementary material. A computer projection of the structure is reproduced in Figure 2.

Acknowledgment. We wish to thank Marilyn M. Olmstead for the X-ray crystal structures and the University of California for partial support of the work by a Faculty Research Grant.

Supplementary Material Available: The relative experimental parameters for the X-ray structure determination of the sulfinamide along with atomic coordinates, isotropic thermal parameters, a listing of the bond distances and bond angles as well as hydrogen atom coordinates for *N*-(1-phenylethyl)-methanesulfinamide and 3-((1-phenylethyl)ammonio)propanesulfinate (7 pages). Ordering information is given on any current masthead page.

Mechanism of Dicyanoanthracene-Photosensitized Oxygenation of 1,1,2,2-Tetraarylcyclopropanes and 1,1,3,3-Tetraarylpropenes

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1,1,2,2-Tetraphenylcyclopropane (**2a**) and electron-donor-substituted 1,1-diaryl-2,2-diphenylcyclopropanes **2b–f** as well as correspondingly substituted 1,1-diaryl-3,3-diphenylpropenes **5a–e** and 3,3-diaryl-1,1-diphenylpropenes **6a–e** were irradiated in CCl_4 and acetonitrile in the presence of oxygen and various sensitizers. The cyclopropanes as well as the propenes are inert toward singlet oxygen in both solvents. In electron-transfer-induced oxygenation reactions, photosensitized by 9,10-dicyanoanthracene in acetonitrile, cyclopropanes **2d–f**, carrying efficient electron-donating 4-methoxyphenyl and 4-phenoxyphenyl groups, yield 1,2-dioxolanes **3d–f** exclusively. Cyclopropanes **2b** and **2c**, which carry less efficient electron-donating 4-methylphenyl groups, give rise to dioxolanes **3b** and **3c**, respectively, as major products. In addition, allylic hydroperoxides **4b** and **4c** are formed, which are further oxygenated to benzophenone (**10**) and the corresponding diaryl ketones **7b** and **7c**. 1,1,2,2-Tetraphenylcyclopropane (**2a**) yields dioxolane **3a** and allylic hydroperoxide **4a** in a ratio of 3:2 as major products; in addition, 1,1,3,3-tetraphenylpropene (**5a** = **6a**) is formed as a minor product that is oxygenated under the reaction conditions to benzophenone (**10**) and diphenylacetaldehyde (**8**). By use of biphenyl (co-sensitizer), lithium perchlorate (special salt effect), and *p*-benzoquinone (quencher of $O_2^{\bullet-}$), it is shown that cyclopropanes **2a–f** are oxygenated in chain reactions involving (1) 1,3-radical cations $\mathbf{2}^{\bullet+}$ rather than 1,3-triplet biradicals and (2) triplet ground-state oxygen rather than the superoxide radical anion. Use of 1,8-dihydroxyanthraquinone as a sensitizer supports these results. Propenes **5a–e** and **6a–e** yield ketones and aldehydes as major products by reactions of 1,2-radical cations $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$ with $O_2^{\bullet-}$ as the oxygenating species. Dioxolanes and allylic hydroperoxides are not produced from these propenes. A mechanism is developed for the electron-transfer-induced photooxygenation of 1,1,2,2-tetraarylcyclopropanes **2** that shows that the increase of the resonance stabilization of the 1,3-radical cation $\mathbf{2}^{\bullet+}$, caused by substitution of phenyl groups by electron-releasing aryl groups and demonstrated by the concomitantly decreasing oxidation potential of **2**, plays the essential role in determining oxygenation rates and product formation.

Introduction

In oxygen- or air-saturated polar solvents, aryl-substituted cyclopropanes (CP) may be converted into 1,2-dioxolanes by photosensitization with 9,10-dicyanoanthracene (DCA)[1,2] or quinones.[3] These conversions proceed by electron-transfer-induced photooxygenation reactions, for which three different mechanisms have been discussed: the first, involving the superoxide radical anion

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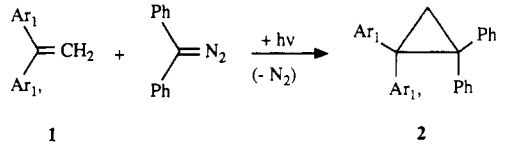
(2) Oxygenation of 1,2-diarylcyclopropanes: (a) Mizuno, K.; Kamiyama, N.; Otsuji, Y. *Chem. Lett.* **1983**, 477. (b) Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron* **1985**, *41*, 2207.

(3) Oxygenation of 2,2-diaryl-1-methylenecyclopropanes: (a) Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6511. (b) Okada, K.; Hisamitsu, K.; Takahashi, Y.; Hanaoka, K.; Miyashi, T.; Mukai, T. *Tetrahedron Lett.* **1984**, *25*, 5311. (c) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079.

0022-3263/90/1955-5945$02.50/0

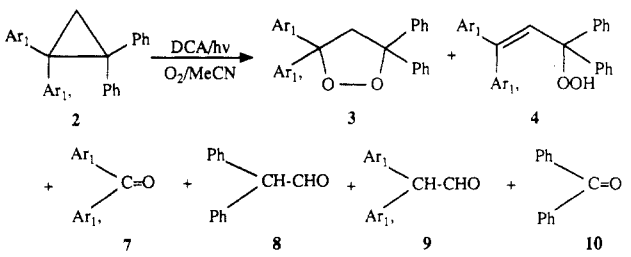
Scheme I. Synthesis of 1,1-Diaryl-2,2-diphenylcyclopropanes



1 2

a: $Ar_1 = Ar_{1'} = C_6H_5$;
b: $Ar_1 = 4\text{-}CH_3\text{-}C_6H_4$, $Ar_{1'} = C_6H_5$;
c: $Ar_1 = Ar_{1'} = 4\text{-}CH_3\text{-}C_6H_4$;
d: $Ar_1 = 4\text{-}CH_3O\text{-}C_6H_4$, $Ar_{1'} = C_6H_5$;
e: $Ar_1 = Ar_{1'} = 4\text{-}CH_3O\text{-}C_6H_4$;
f: $Ar_1 = Ar_{1'} = 4\text{-}C_6H_5O\text{-}C_6H_4$.

Scheme II. DCA-Photosensitized Oxygenation of 1,1-Diaryl-2,2-diphenylcyclopropanes



2 3 4 7 8 9 10

Table I. Oxidation Potentials, E_{ox}, and DCA Fluorescence Quenching Constants, k_q, of 1,1-Diaryl-2,2-diphenylcyclopropanes in Acetonitrile

2	R[a] in Ar$_1$	R[a] in Ar$_{1'}$	E_{ox}[b] (V)	k_q, exp[c] (10^{10}/M s)	ΔG, calcd[d] (kcal/mol)	k_q, calcd[e] (10^{10}/M s)
a	H	H	1.37	1.06	−15.7	1.37
b	CH_3	H	1.20	1.18	−19.6	1.42
c	CH_3	CH_3	1.16	1.33	−20.5	1.43
d	CH_3O	H	1.09	1.34	−22.1	1.44
e	CH_3O	CH_3O	1.09	1.54	−22.1	1.44
f	C_6H_5O	C_6H_5O	1.07	1.48	−22.6	1.44

[a] Ar = 4-R-C_6H_4. [b] Irreversible oxidation potentials in MeCN (vs SCE); scan rate 400 mV/s; standard 1,3,5-trimethoxybenzene, $E_{ox}^{1/2} = 1.49$ V.[12] [c] From fluorescence quenching (see text). [d] $\Delta G = 23.06\ [E_{ox}(2) - E_{red}^{1/2}(DCA) - e_0^2/\epsilon r - E_{0,0}(DCA)]$, with $e_0^2/\epsilon r = 0.06$ eV, $E_{red}^{1/2}(DCA) = -0.89$ V, and $E_{0,0}(DCA) = 2.88$ eV.[13] [e] $k_q = (2 \times 10^{10})[1 + 0.25[\exp(\Delta G^{\ddagger}/RT) + \exp(\Delta G/RT)]]^{-1}$ M^{-1} s^{-1} in MeCN (20 °C), with $\Delta G^{\ddagger} = \Delta G/2 + [(\Delta G/2)^2 + (\Delta G^{\ddagger}(0))^2]^{1/2}$ and $\Delta G^{\ddagger}(0) = 2.4$ kcal/mol.[14]

$O_2^{\bullet-}$, proceeds according to reactions 1–4,[1a,b] the second occurs as a chain reaction in which ground-state molecular oxygen ($^3O_2$) participates (reactions 1, 2, 5–7),[1c,2,3] and the third proceeds via a triplet 1,3-biradical intermediate formed by an electron return to the 1,3-radical cation according to reaction 8 in the sequence of reactions 1, 2, 8, and 9.[4]

$$DCA + h\nu \rightarrow {}^1DCA^* \quad (1)$$

$$^1DCA^* + CP \rightarrow DCA^{\bullet-} + CP^{\bullet+} \quad (2)$$

$$DCA^{\bullet-} + {}^3O_2 \rightarrow DCA + O_2^{\bullet-} \quad (3)$$

$$CP^{\bullet+} + O_2^{\bullet-} \rightarrow \text{1,2-dioxolane} \quad (4)$$

$$CP^{\bullet+} + {}^3O_2 \rightarrow (CPO_2)^{\bullet+} \quad (5)$$

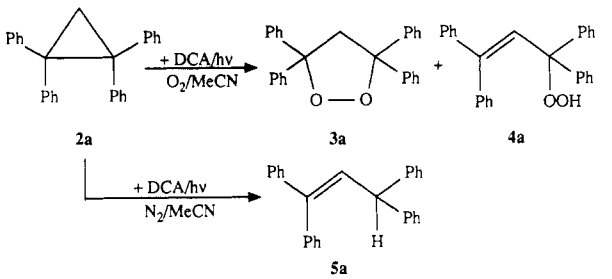
$$(CPO_2)^{\bullet+} + CP \rightarrow \text{1,2-dioxolane} + CP^{\bullet+} \quad (6)$$

$$(CPO_2)^{\bullet+} + DCA^{\bullet-} \rightarrow \text{1,2-dioxolane} + DCA \quad (7)$$

$$CP^{\bullet+} + DCA^{\bullet-} \rightarrow \uparrow^{\bullet}CP^{\bullet}\uparrow + DCA \quad (8)$$

$$\uparrow^{\bullet}CP^{\bullet}\uparrow + {}^3O_2 \rightarrow \text{1,2-dioxolane} \quad (9)$$

Of the cyclopropanes studied so far, 1,1,2,2-tetraphenylcyclopropane (**2a**) appears to exhibit a unique behavior in reactions photosensitized by cyanoaromatics: under nitrogen, it rearranges to 1,1,3,3-tetraphenylpropene (**5a**),[5] whereas under oxygen, allylic hydroperoxide **4a** is formed in substantial amounts in addition to 1,2-dioxolane **3a**.[1a,b]



2a 3a 4a 5a

DCA is a sensitizer for electron-transfer-induced photooxygenations as well as for singlet oxygen ($^1O_2$) reactions.[6-8] Allylic hydroperoxide **4a** could therefore originate from propene **5a** by either photooxygenation reaction (or both), if the rearrangement of **2a** to **5a** can compete with the photoooxygenation of **2a**.

Replacement of phenyl groups by electron-donor-substituted aryl groups such as 4-methoxyphenyl in 1,2-diarylcyclopropanes provoked a significant increase of the oxygenation rates and the yields of dioxolane formation.[2b]

In order to gain more insight into the behavior of tetraaryl-substituted cyclopropanes in DCA-photosensitized oxygenation reactions, we studied some 1,1-diaryl-2,2-diphenylcyclopropanes (**2a–f**) (present study) as well as a series of 1,1,2,3-tetraarylcyclopropanes (accompanying paper).[9] In addition, we compared their reactivities toward singlet oxygen and their electron-transfer-induced photooxygenation reactions with those of the correspondingly 1,1,3,3-tetraaryl-substituted propenes (**5a–e**, **6b–e**).

Results

Synthesis of 1,1-Diaryl-2,2-diphenylcyclopropanes. 1,1-Diaryl-2,2-diphenylcyclopropanes **2a–f** were prepared by the well-known procedure of diphenylcarbene cycloaddition to ethylenes.[10] In order to achieve this reaction, we photolyzed diphenyldiazomethane in deoxygenated benzene solution in the presence of 1,1-diarylethylenes **1a–f** (Scheme I). 1,1,3,3-Tetraarylpropenes **5** and **6** were prepared as described in the accompanying paper.[9]

Oxidation Potentials of 1,1-Diaryl-2,2-diphenylcyclopropanes and 1,1,3,3-Tetraarylpropenes. DCA Fluorescence Quenching by 1,1-Diaryl-2,2-diphenyl-

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Table II. DCA-Photosensitized Oxygenation of 1,1-Diaryl-2,2-diphenylcyclopropanes in Oxygen-Saturated Acetonitrile[a]

	R[c] in					products after t^f	
2[b]	Ar_1	$Ar_{1'}$	add.[d]	t_0[e] (h)	t^f (h)	3 (%)	others (%)
a	H	H		8	14[g]	40	25[h]
			Bp		2	70	30[i]
b	Me	H		3	22	70	30[j]
			Bp		1.7	≥90	≤10[j]
			Bq	0.5	10	70	30[j]
c	Me	Me			7	90	10[k]
			Bp		1.7	100	
			Lp		5	90	10[k]
			Bq		10	90	10[k]
			l	1	20	90	10[k]
d	OMe	H		0.5	1.1	100	
			Bp		0.3	100	
			Lp		0.3	100	
			Bq		1.7	100	
			l	1	18	100	
e	OMe	OMe		0.3	0.8	100	
			Bp		0.3	100	
			Bp[m]		0.8	100	
			Lp		0.3	100	
			Lp[n]		0.3	100	
			Bq		1	100	
			l	2	5	100	
f	OPh	OPh			0.3	100	
			Bp		0.2	100	
			Lp		0.2	100	
			Bq		0.7	100	
			l	2	7	100	

[a] Irradiations carried out at room temperature in the 25-mL irradiation unit (see Experimental Section). [b] Initial concentration: 0.025 M. [c] Ar = 4-R-C_6H_4. [d] Bp = biphenyl; Lp = $LiClO_4$; Bq = *p*-benzoquinone; concentration of additive 0.025 M. [e] Induction period. [f] Time required for the consumption of 1 molar equiv of O_2 (induction period included). [g] The reaction mixture contained still 35% of **2a**. [h] **4a** (major) and **8** + **10** (minor 1:1); for product distribution after 3 molar equiv of O_2 were consumed; see text. [i] Mainly **10** + unknown compound (δ 5.7). [j] **10** and **7b**. [k] **10** and **7c**. [l] Sensitizer 1,8-dihydroxyanthraquinone, 3×10^{-4} M. [m] [Bp] = 0.003 M. [n] [Lp] = 0.013 M.

cyclopropanes. Oxidation potentials of 1,1-diaryl-2,2-diphenylcyclopropanes **2a–f** (Table I) and of 1,1,3,3-tetraarylpropenes **5a–e** and **6b–e** (Table III) were determined in acetonitrile (MeCN) solutions by cyclic voltammetry.

Quenching of DCA fluorescence by cyclopropanes **2a–f** was executed for nitrogen-saturated MeCN solutions. DCA was excited at 383 nm; the intensities of the DCA fluorescence emission at 450 nm were determined for at least six different concentrations of the respective cyclopropane (between 0.002 and 0.03 M). Fluorescence quenching constants k_q were obtained from the slopes of Stern–Volmer plots, $k_q\tau_{DCA}$, with τ_{DCA} = 15.3 ns in MeCN,[11] by applying the method of the least squares (Table I).

Because the oxidation potentials of **2a–f** are irreversible, the ΔG values calculated by using the Rehm–Weller equation[14] should be merely approximate. However, they seem to agree quite well with experiment,[8,15] as is demonstrated by the satisfying agreement of the experimentally observed fluorescence quenching constants with those calculated.

Table III. DCA-Photosensitized Oxygenation of 1,1,3,3-Tetraarylpropenes 5 and 6 in Oxygen-Saturated Acetonitrile[a]

	R[b] in		E_{ox}[c]		r_0[e]		propene reacted
	Ar_1	$Ar_{1'}$	(V)	add.[d]	mL/min	t^f (h)	(%)
5a	H	H	1.71		0.10	2.0	45
(= **6a**)				Bp	0.15	1.3	45
5b	Me	H	1.65		0.10	2.0	45
				Bp	0.11	1.7	45
				Bq		*g*	0
				Bq[h]		*g*	0
6b	Me	H	1.72	Bp	0.11	1.7	45
5c	Me	Me	1.62	Bp	0.09	2.3	45
6c	Me	Me	1.67	Bp	0.11	1.7	47
5d	OMe	H	1.42	Bp	0.08	2.6	42
6d	OMe	H	1.65	Bp	0.08	2.7	38
5e	OMe	OMe	1.38	Bp	0.08	2.6	41
6e	OMe	OMe	1.63	Bp	0.05	4.4	40

[a] **5** and **6** (0.025 M) were irradiated at room temperature in the 25-mL irradiation unit (see Experimental Section). [b] Ar = 4-R-C_6H_4. [c] Irreversible oxidation potentials in MeCN (vs SCE); scan rate 400 mV/s; standard 1,3,5-trimethoxybenzene, $E_{ox}^{1/2}$ = 1.49 V.[12] [d] Bp = biphenyl; [Bp] = 0.025 M; Bq = *p*-benzoquinone; [Bq] = 0.025 M. [e] Initial rate of oxygen consumption. [f] Time required for the consumption of 1 molar equiv of O_2. [g] No O_2 consumption occurred during 6 h of irradiation. [h] [Bq] = 0.003 M.

1,8-Dihydroxyanthraquinone (1,8-AQ) was also used as a sensitizer (see below, and Tables II and III). With $E_{red}^{1/2}$ = −0.64 V and $E_{0,0}$ = 2.49 eV for the singlet excited state of 1,8-AQ, ^{1}(1,8-AQ)*, in MeCN,[16] $\Delta G \leq 0$ is calculated for substrates whose oxidation potential E_{ox} is less than 1.9 V. Electron transfer between ^{1}(1,8-AQ)* and cyclopropanes **2b–f** should therefore occur with rates about as fast as those with ^{1}DCA*.[17]

Irradiation of 1,1-Diaryl-2,2-diphenylcyclopropanes in Oxygen-Saturated Solutions of CCl_4 and Acetonitrile in the Presence of Various Sensitizers. In order to explore the reactivity of cyclopropanes **2a–f** toward singlet oxygen ($^1O_2$) and in electron-transfer-induced photooxygenations, we used a 25-mL irradiation unit with automatic registration of O_2 consumption as was developed in our laboratory by Paur.[19] The cyclopropanes were irradiated in oxygen-saturated solutions of CCl_4 in the presence of tetraphenylporphin (TPP) and DCA, as well as in O_2-saturated MeCN solutions in the presence of rose bengal (RB), DCA, or 1,8-AQ as sensitizers. For DCA-photosensitized reactions in MeCN, the co-sensitizing effect of biphenyl,[1a,b,20] the special salt effect of lithium perchlorate,[21] and the quenching effect of *p*-benzoquinone on $O_2^{\bullet-}$ [22] were studied.

In CCl_4, the cyclopropanes did not consume any oxygen during several hours of irradiation in the presence of TPP

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or DCA. According to the ^1H NMR spectra, the cyclopropanes remained unchanged under these conditions. TPP and DCA are both efficient sensitizers for the generation of $^1O_2$ in CCl_4.[8] Thus, as expected, not only 1,1,2,2-tetraphenylcyclopropane (**2a**)[1a,b] but also electron-donor-substituted 1,1,2,2-tetraarylcyclopropanes **2b–f** proved inert toward singlet oxygen.

In *MeCN*, no oxygen uptake was observed when cyclopropanes **2a–f** were irradiated for several hours in the presence of RB. Again, the cyclopropanes remained unchanged (^1H NMR) under these conditions. This result agrees well with the inertness of the cyclopropanes toward singlet oxygen as observed above for CCl_4 solutions.

However, if DCA or 1,8-AQ were used as sensitizers in MeCN solutions, cyclopropanes **2a–f** were slowly photooxygenated.

The following results were obtained when DCA was used as a sensitizer.

With **2a** and **2b**, O_2 consumption occurred after a rather long induction period (see Table II). But once the oxygenation started, oxygen was consumed well beyond 1 molar equiv, for example, with **2a** to better than 3 mol of O_2. When the reaction of **2a** was interrupted after 1 mol of O_2 was absorbed, the reaction mixture contained still about 35% of cyclopropane **2a**. According to ^1H NMR analysis, dioxolane **3a** (singlet of the CH_2 protons at δ 4.08) and allylic hydroperoxide **4a** (singlet of the olefinic H at δ 6.85) were formed in a 3:2 ratio.[23] When we stopped the oxygen uptake after 1.6 mol of O_2 were consumed, benzophenone (**7a** = **10**) and diphenylacetaldehyde (**8** = **9a**; two doublets at δ 4.80 and 9.81, J = 2.5 Hz)[25] appeared in the product mixture in a ratio of about 1:1, in addition to cyclopropane **2a**, dioxolane **3a**, and allylic hydroperoxide **4a**. When we finally stopped the reaction after consumption of 3 mol of O_2, cyclopropane **2a** was almost used up (to $\leq$ 5% of the starting amount of **2a**). The reaction mixture now contained dioxolane **3a** and benzophenone (**10**) as main components, and only some allylic hydroperoxide **4a** and diphenylacetaldehyde (**8**); the ratio of compounds **10**:**8** was about 5:1. At least one additional product had been formed, which exhibited a singlet at δ 5.7 (Scheme II).

With cyclopropanes **2b** and **2c**, the major products were 1,2-dioxolanes **3b** and **3c**, respectively. The minor products were identified as benzophenone (**10**) (from both cyclopropanes), 4-methylbenzophenone (**7b**), and 4,4′-dimethylbenzophenone (**7c**). The corresponding allylic hydroperoxides **4b** and **4c** as well as diphenylacetaldehyde (**8**) and the corresponding diarylaldehydes **9b** and **9c** could not be detected.

Cyclopropanes **2d–f**, substituted with one or two more strongly electron-donating aryl groups, yielded 1,2-dioxolanes **3d–f** exclusively.

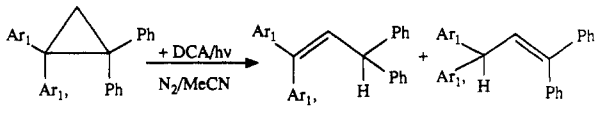
Addition of biphenyl (Bp) shortens the induction period and enhances the oxygenation rates appreciably, and it seems to favor the formation of dioxolanes **3a–c** over the other oxidation products. Addition of lithium perchlorate (Lp) shows similar effects. Addition of benzoquinone (Bq) has in general only little effect on the oxygenation rate as well as on the product distribution. The inability of Bq to quench the oxygenation of the cyclopropanes, even if applied at a rather high concentration, is especially noteworthy.

The use of 1,8-AQ as a sensitizer results in prolonged induction periods and in appreciably decreased oxygenation rates as compared to those obtained with DCA.

Preparation of 1,2-Dioxolanes from 1,1-Diaryl-2,2-diphenylcyclopropanes. In order to obtain appreciable amounts of 1,2-dioxolanes **3a–f**, we irradiated cyclopropanes **2a–f** in a 200-mL irradiation unit with DCA as a sensitizer in oxygen-saturated solutions of MeCN. To shorten the irradiation period when cyclopropanes **2a** and **2b** were used, biphenyl or $LiClO_4$ was added. A filter solution (see Experimental Section) used to cut-off wavelengths shorter than 405 nm avoided electronic excitation of the cyclopropanes and their oxygenation products. The progress of reaction was followed by ^1H NMR analyses of samples drawn during the irradiation period. Isolation and characterization of the dioxolanes, of which **3a**[1a,b] and **3c–e**[1c] have been obtained earlier, were carried out as described in the Experimental Section.

Irradiation of 1,1-Diaryl-2,2-diphenylcyclopropanes in Nitrogen-Saturated MeCN Solutions in the Presence of DCA and Other Sensitizers. Cyclopropanes **2c–f** proved to be stable toward irradiation for several hours (>15 h) in N_2-saturated MeCN solutions in the presence of DCA. Moreover, cyclopropane **2d** was stable when irradiated for >15 h in the presence of 1,4-dicyanonaphthalene (DCN, $E_{red}^{1/2}$ = −1.28 V[13]) and 1,8-AQ as sensitizers.

Under similar conditions, cyclopropanes **2a** and **2b** rearranged quantitatively within 15 h to 1,1,3,3-tetraphenylpropene (**5a** = **6a**) and 1-(4-methylphenyl)-1,3,3-triphenylpropene (**5b**),[26] respectively, when DCA and DCN were used as sensitizers. Under the same conditions, but with 1,8-AQ as a sensitizer, neither **2a** nor **2b** were rearranged within 30 h.



2 5 6

Irradiation of 1,1,3,3-Tetraarylpropenes in Oxygen-Saturated Solutions of CCl_4 and MeCN in the Presence of Various Sensitizers. No oxygen consumption occurred when tetraarylpropenes **5a–e** and **6b–e** were irradiated for several hours in O_2-saturated solutions of CCl_4 and MeCN in the presence of sensitizers TPP and RB, respectively. According to the ^1H NMR spectra, **5a–e** and **6b–e** remained unchanged. These results show that 1,1,3,3-tetraarylpropenes are inert toward singlet oxygen.[27]

(23) The allylic hydroperoxide was not isolated. The assignment is based on the assumption that the olefinic H at δ 6.85 is due to this compound because the corresponding alcohol, 3-hydroxy-1,1,3,3-tetraphenylpropene, prepared according to ref 24, exhibits a singlet for its olefinic H at δ 6.81.

(24) Ubbelohde, A. R.; Burgess, J. A. *J. Chem. Soc. B* **1970**, 1106.

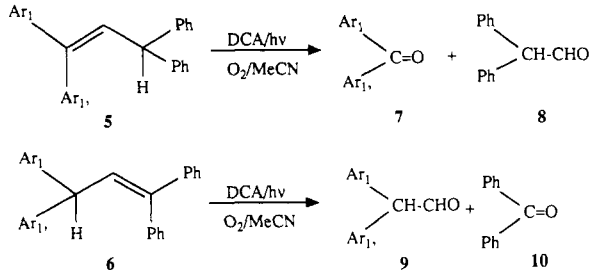
(25) Reduction of the reaction mixture yielded benzhydrol and 2,2-diphenylethanol, proving the assignment made by ^1H NMR analysis.

(26) **5b** is formed in two configurational isomers, the *E* and *Z* form, which exhibit both their vinyl protons as doublets at δ 6.50, their allylic protons, however, as doublets at δ 4.78 and 4.83, J = 10 Hz. Since the structural isomer 3-(4-methylphenyl)-1,1,3-triphenylpropene (**6b**) exhibits its vinyl and allylic protons as doublets at δ 6.51 and 4.78, J = 10 Hz, i.e., at positions where either (*E*)- or (*Z*)-**5b** absorbs, the occurrence of **6b** as a rearrangement product of **2b** is uncertain.

(27) One might expect that a 1,1,3,3-tetraarylpropene, containing an allylic hydrogen, should undergo an ene reaction with singlet oxygen.[28] However, as with 1,1-dimethyl-2-isopropylethylene, the tertiary allylic hydrogen atom may not be suited for this reaction. Due to steric interactions between the four phenyl groups, the C–H bond should be forced into the most unfavorable position for an ene reaction, i.e., perpendicular to the π-bond of the adjacent C–C double bond (compare ref 28, p 320). Wayner and Arnold[29] have pointed out that the observed vicinal ^1H–^1H coupling constant of 10 Hz for the allylic (δ 4.75) and the vinyl proton (δ 6.45) is evidence for this preferred conformation. Tetraarylpropenes **5a–e** and **6b–e** all show doublets at δ 4.75 ± 0.05 and 6.42 ± 0.05 with coupling constants of 10 to 11 Hz.[9,26]

(28) Gollnick, K.; Kuhn, H. J. in *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 287.

Scheme III. DCA-Photosensitized Oxygenation of 1,1,3,3-Tetraarylpropenes



However, photooxygenation does proceed in O_2-saturated MeCN solutions if DCA is used as a sensitizer, though rather slowly. In the presence of biphenyl (Bp) as a co-sensitizer, the reaction time is appreciably shortened, but the products are the same as obtained in the absence of Bp. In contrast to the oxygenation of cyclopropanes **2**, that of propene **5b** (and probably those of the other propenes of Table III as well) is totally quenched by addition of even rather small amounts of benzoquinone.

5a–e afforded ketones **7a–e** and diphenylacetaldehyde (**8**) as major components of the product mixtures, whereas **6b–e** delivered benzophenone (**10**) and diarylacetaldehydes **9b–e** as major products. Though we made no attempt to elucidate the structures of the minor products, we looked carefully for the appearance of allylic hydroperoxides **4** (and of dioxolanes **3** as well) during the reaction by drawing samples from time to time. These samples were analyzed for the appearance of the distinctive protons expected to arise as singlets at about δ 6.8 and δ 4.0 in the ^{1}H NMR spectra of allylic hydroperoxides **4** and 1,2-dioxolanes **3**, respectively. However, these compounds were obviously not generated at any time of the reactions (Scheme III).

Discussion

1,1,2,2-Tetraarylcyclopropanes **2a–f** (= Cp) are inert toward singlet oxygen. They are, however, readily oxygenated in electron-transfer-induced reactions when suitable sensitizers such as DCA or 1,8-AQ are applied. The rate of oxygenation steadily decreases during the irradiation. This decrease is a consequence of our experimental arrangement: we keep the oxygen concentration constant by replacing O_2 that is consumed during the reaction by oxygen from the burette; Cp, however, is continuously consumed by the oxygenation. Due to reactions 2 (see above) and 10[6,8] the competition of Cp and $^3O_2$ for

$$^1DCA^* + {}^3O_2 \rightarrow {}^3DCA^* + {}^1O_2 \qquad (10)$$

^{1}DCA* becomes constantly more unfavorable for Cp when the reaction proceeds.

The rate-enhancing effect of the co-sensitizer biphenyl (Bp) and that of the special salt effect of $LiClO_4$ (Lp) support the view that an electron-transfer-induced process prevails. The presence of Bp increases the actual concentration of the intermediate free radical cation $Cp^{\bullet+}$ because of several reasons: (1) Bp is not consumed during the reaction (or at least to a much lesser extent than Cp) so that the competition between Bp and $^3O_2$ for ^{1}DCA* is kept constant throughout the oxygenation reaction of Cp; (2) $Bp^{\bullet+}$, generated by reaction 11 reacts readily by secondary electron transfer according to step 12

$$^1DCA^* + Bp \rightarrow DCA^{\bullet-} + Bp^{\bullet+} \qquad (11)$$

$$Bp^{\bullet+} + Cp \rightarrow Bp + Cp^{\bullet+} \qquad (12)$$

since E_{ox}(Bp) = 1.85 V[30] is larger than any E_{ox}(Cp); and (3), because $Cp^{\bullet+}$ is produced in reaction 12 without a counterion radical (in contrast to reaction 2), back electron transfer does not decrease the chance for $Cp^{\bullet+}$ to react further to oxygenation products.

The special salt effect of Lp[21] rests on the partial prevention of the back electron transfer between $Cp^{\bullet+}$ and $DCA^{\bullet-}$ (to give Cp and DCA) in that Li^+ traps $DCA^{\bullet-}$ and thus increases the concentration of free $Cp^{\bullet+}$ that reacts to products.

The rate-enhancing effects of Bp and Lp both argue against the participation of triplet biradicals $\uparrow^{\bullet}Cp^{\bullet}\uparrow$ in the oxygenation process. Since the formation of such biradicals rests on the back electron transfer from $DCA^{\bullet-}$ to $Cp^{\bullet+}$ within the primary radical ion pair, $(DCA^{\bullet-}/Cp^{\bullet+})$, and according to reaction 8, Bp and Lp should decrease rather than increase the rate of oxygenation if $\uparrow^{\bullet}Cp^{\bullet}\uparrow$ were the essential intermediate that reacts with $^3O_2$ to oxygenation products such as 1,2-dioxolanes **3** (= CpO_2).

Braun[22a] and Foote[22b] have recently shown that *p*-benzoquinone (Bq) ($E_{red}^{1/2}$ = −0.51 V[31]) is an efficient quencher of $O_2^{\bullet-}$. With $E_{red}^{1/2}(O_2)$ = −0.78 V and $E_{red}^{1/2}$(DCA) = −0.89 V,[13] Bq should readily undergo a secondary electron transfer not only with $O_2^{\bullet-}$ (reaction 13) but also with $DCA^{\bullet-}$ (reaction 14). The latter reaction

$$O_2^{\bullet-} + Bq \rightarrow O_2 + Bq^{\bullet-} \qquad (13)$$

$$DCA^{\bullet-} + Bq \rightarrow DCA + Bq^{\bullet-} \qquad (14)$$

should, however, not increase the actual $Cp^{\bullet+}$ concentration because one radical anion ($DCA^{\bullet-}$) is only replaced by another ($Bq^{\bullet-}$). Since back electron transfer from $Bq^{\bullet-}$ to $Cp^{\bullet+}$ should be approximately as effective as from $DCA^{\bullet-}$, the oxygenation rate should nearly be unaffected by reaction 14.

Due to reaction 13, Bq should quench, however, any electron-transfer-induced oxygenation reaction that proceeds via $O_2^{\bullet-}$ as an intermediate. Since Bq does not prevent the photooxygenation of Cp even if applied at rather high concentrations (Table II), these results argue against the participation of $O_2^{\bullet-}$ in the product-forming step. Because reaction 4 is thus excluded, production of oxygenation products CpO_2 should occur with $^3O_2$ in a chain reaction according to reaction steps 5 and 6, with reaction 7 or, more probably, with reaction 15 as a chain-terminating step.

$$(CpO_2)^{\bullet+} + O_2^{\bullet-} \rightarrow CpO_2 + O_2 \qquad (15)$$

Electron transfer from Cp to $(CpO_2)^{\bullet+}$ (reaction 6) is exergonic since $E_{ox}(CpO_2)$ is always much larger than E_{ox}(Cp), e.g., E_{ox}(**2a**) = 1.37 V, E_{ox}(**3a**) = 1.98 V, E_{ox}(**2e**) = 1.09 V, E_{ox}(**3e**) = 1.66 V. Reactions 6, 7, and 15 should all proceed with approximately diffusion-controlled rates, i.e., the relative rates should be proportional to the concentrations of Cp, $DCA^{\bullet-}$, and $O_2^{\bullet-}$. Since [Cp] is several orders of magnitude larger than the concentrations of the short-lived intermediates $DCA^{\bullet-}$ and $O_2^{\bullet-}$, there is little doubt that CpO_2 is formed in a chain reaction mechanism involving triplet ground-state oxygen.

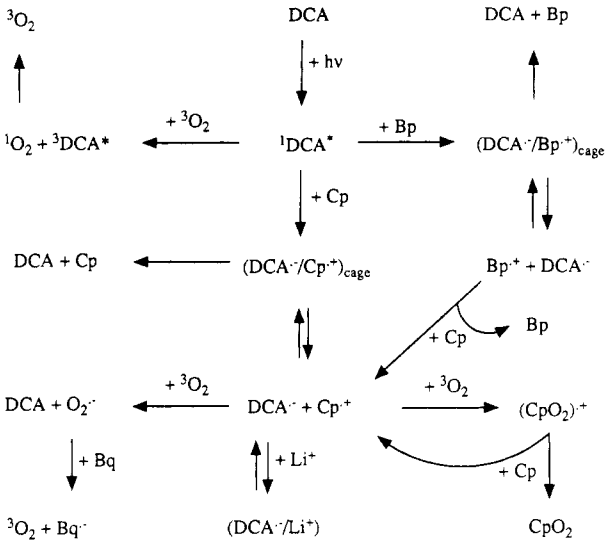
The suitability of 1,8-AQ as a sensitizer supports this assertion. We have recently shown that 1,8-AQ is a sensitizer for electron-transfer-induced photooxygenations that proceed via $^3O_2$; those proceeding via $O_2^{\bullet-}$, however, cannot be sensitized by 1,8-AQ because its reduction po-

(29) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 871.

(30) Osa, T.; Yildiz, A.; Kuwana, T. *J. Am. Chem. Soc.* **1969**, *91*, 3394.

(31) Mann, C. K.; Barness, K. K. *Electrochemical Reactions in Nonaqueous Solutions*; Marcel Dekker, Inc.: New York, 1970.

Scheme IV. Electron-Transfer-Induced Oxygenation of 1,1,2,2-Tetraarylcyclopropanes. Rate Enhancement by Co-sensitizer Biphenyl and by the Special Li Salt Effect



tential of $E_{red}^{1/2} = -0.64$ V is less negative than that of O_2, thus preventing 1,8-AQ$^{\bullet-}$ from transferring its extra electron to $^3O_2$.[32]

Scheme IV summarizes the results so far obtained, with Cp = 1,1,2,2-tetraarylcyclopropanes **2** and CpO_2 = 3,3,5,5-tetraaryl-1,2-dioxolanes **3**.

Cyclopropanes, carrying one (**2d**) or two (**2e,f**) strongly electron-donating aryl groups, afford dioxolanes **3d–f** exclusively. Dioxolanes **3a–c** represent the main products from cyclopropanes **2a–c**.

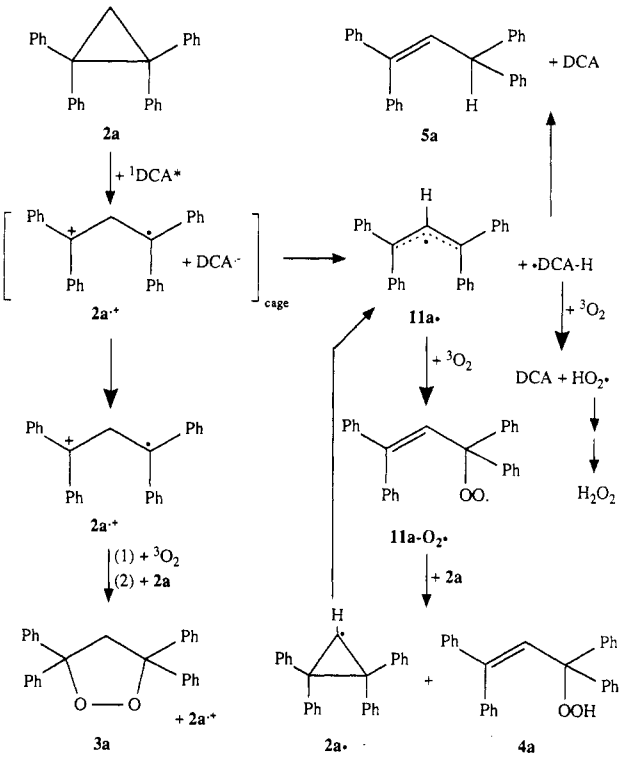
However, in addition to dioxolane **3a**, **2a** yields the allylic hydroperoxide **4a** in substantial amounts if the photooxygenation is interrupted when 1 molar equiv of O_2 is consumed. Furthermore, benzophenone (**10**) and diphenylacetaldehyde (**8**) appear at a ratio of about 1:1 as minor products in the reaction mixture. Continuation of the reaction leads to an increase in the amount of dioxolane **3a** as well as of benzophenone (**10**), the latter obviously formed at the expense of allylic hydroperoxide **4a**. After finally about 3 molar equiv of O_2 are consumed, dioxolane **3a** and benzophenone (**10**) represent the predominant products, whereas diphenylacetaldehyde (**8**) and allylic hydroperoxide **4a** have become rather minor products.

It is tempting to assume that **2a** is photorearranged to 1,1,3,3-tetraphenylpropene (**5a**), which is subsequently photooxygenated to **4a**, either by an ene reaction with singlet oxygen or by an electron-transfer-induced oxygenation reaction. However, the inertness of **5a** towards $^1O_2$ excludes the singlet oxygen pathway. The other pathway is also excluded, because of the absence of even traces of **4a** in the samples drawn during the DCA-photosensitized oxygenation of **5a** in MeCN.

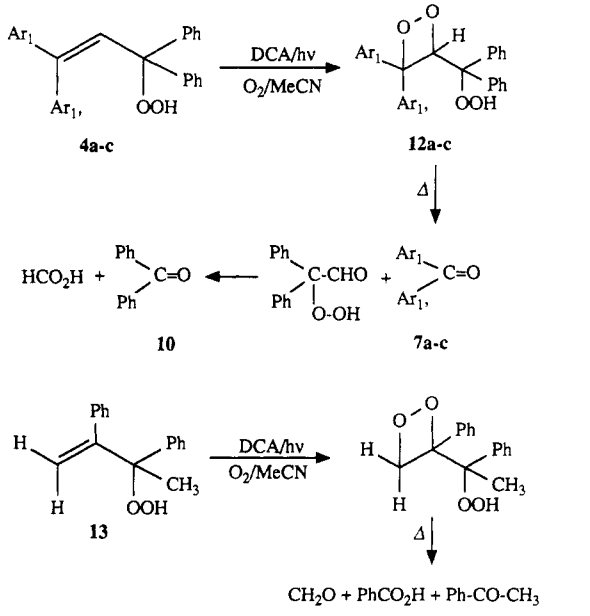
Wayner and Arnold[29] have recently shown that in MeCN, DCA$^{\bullet-}$ may serve as a base in a proton transfer from **2a**$^{\bullet+}$, yielding the allylic radical **11a**$^\bullet$ and $^\bullet$DCA-H.

For this reaction to occur in O_2-saturated MeCN solutions, proton transfer has to take place in the primary radical ion pair, since free DCA$^{\bullet-}$ will immediately be trapped by $^3O_2$, affording DCA and $O_2^{\bullet-}$. Radical **11a**$^\bullet$ will then react with $^3O_2$ to the allylic hydroperoxy radical **11a**–$O_2^\bullet$, presumably with a nearly diffusion-controlled rate. The hydroperoxy radical will finally abstract a hydrogen atom from cyclopropane **2a** to yield the allylic hydroperoxide **4a** and the cyclopropyl radical **2a**$^\bullet$. Rearrangement of the latter to allylic radical **11a**$^\bullet$ provides for the occurrence of a chain reaction so that formation of **4a** can compete with the chain reaction that yields dioxolane **3a**. Since rearrangement of **2a**$^\bullet$ to **11a**$^\bullet$ is rather exergonic ($\Delta G = -39 \pm 3$ kcal/mol[29]), this process may be so fast that **2a**$^\bullet$ can hardly be trapped by $^3O_2$.[33]

Scheme V. Formation of 3,3,5,5-Tetraphenyl-1,2-dioxolane, 3-Hydroperoxy-1,1,3,3-tetraphenylpropene, and 1,1,3,3-Tetraphenylpropene from 1,1,2,2-Tetraphenylcyclopropane



Scheme VI. DCA-Photosensitized Oxygenation of Allylic Hydroperoxides



(32) Gollnick, K.; Schnatterer, A.; Utschick, G.; Paulmann, U.; Held, S. In *Light in Biology and Medicine*, Vol. 1; Douglas, R. H., Moan, J., Dall'Acqua, F., Eds.; Plenum Press: New York, 1988; p 67.

(33) Studies on the behavior of aryl-substituted cyclopropyl radicals in the presence of O_2 are under way.

The mechanism proposed in Scheme V is supported by the effect of the co-sensitizer biphenyl (Bp) on the product ratio of dioxolane **3a** over allylic hydroperoxide **4a**. Because $Bp^{\bullet+}$ generates free $\mathbf{2a}^{\bullet+}$, and since MeCN is apparently not an efficient proton acceptor,[29] dioxolane formation is favored over the formation of **4a** in the presence of Bp.

When the reaction proceeds (in the absence as well as in the presence of Bp), benzophenone (**10**) is formed at the expense of allylic hydroperoxide **4a** (Scheme VI). Dioxetane **12a**, formed by an electron-transfer-induced oxygenation rather than by a [2 + 2]-cycloaddition of singlet oxygen to **4a**, is a reasonable candidate as a precursor for the additional benzophenone formation.[34] A similar reaction was recently observed with allylic hydroperoxide **13**.[8]

Similarly, the occurrence of benzophenone and the respective 4-methyl-substituted benzophenones **7b** and **7c** from **2b** and **2c** (Table II) should be due to the intermediate formation of allylic hydroperoxides **4b** and **4c**, respectively. Substitution of one or two phenyl groups of **2a** by *p*-tolyl groups should give rise to enhanced resonance stabilization of the radical cations $\mathbf{2b}^{\bullet+}$ and $\mathbf{2c}^{\bullet+}$ as compared to radical cation $\mathbf{2a}^{\bullet+}$, which results in less effective proton transfer to $DCA^{\bullet-}$. Furthermore, allylic hydroperoxides **4b** and **4c** should be somewhat better electron donors than **4a** so that **4b** and **4c** should undergo further oxygenation faster than **4a**. Consequently, the concentrations of **4b** and **4c** should always be too low (<3–5%) in the product mixtures to be detected by ^1H NMR analysis with certainty.

During the early stage of DCA-photosensitized oxygenation of **2a**, benzophenone (**10**) and diphenylacetaldehyde (**8**) appear as minor products at a ratio of about 1:1. This result indicates that some rearrangement of **2a** into 1,1,3,3-tetraphenylpropene (**5a**) occurs, the latter being subsequently oxygenated to **8** + **10**, probably via an intermediate 1,2-dioxetane (compare Scheme III).

Wayner and Arnold[29] have shown that in MeCN/methanol solutions, the rearrangement of **2a** proceeds via allylic radical $\mathbf{11a}^{\bullet}$, formed by proton transfer from $\mathbf{2a}^{\bullet+}$ to $DCA^{\bullet-}$ according to reaction 16 followed by reduction

$$DCA^{\bullet-} + \mathbf{2a}^{\bullet+} \rightarrow \text{H-DCA}^{\bullet} + \mathbf{11a}^{\bullet} \quad (16)$$

of $\mathbf{11a}^{\bullet}$ by another $DCA^{\bullet-}$ to give DCA and allylic anion $\mathbf{11a}^{-}$ (reaction 17) that is subsequently protonated to **5a** by methanol.

$$DCA^{\bullet-} + \mathbf{11a}^{\bullet} \rightarrow DCA + \mathbf{11a}^{-} \quad (17)$$

In oxygen-saturated MeCN solutions, however, reaction 17 is rather unlikely to occur, because free $DCA^{\bullet-}$ is almost quantitatively trapped by O_2 to yield DCA and $O_2^{\bullet-}$. Whereas reduction of $\mathbf{11a}^{\bullet}$ ($E_{red}^{1/2}(\mathbf{11a}^{\bullet})$ = −0.94 V vs SCE)[29] by $DCA^{\bullet-}$ ($E_{red}^{1/2}(DCA)$ = −0.89 V vs SCE)[13] is just still feasible, superoxide radical anion $O_2^{\bullet-}$ ($E_{red}^{1/2}(O_2)$ = −0.78 V vs SCE)[13] should no longer be able to transfer an electron to $\mathbf{11a}^{\bullet}$. However, H-atom transfer from H-DCA$^{\bullet}$ to $\mathbf{11a}^{\bullet}$ to give DCA + **5a** (reaction 18) should readily occur

$$\text{H-DCA}^{\bullet} + \mathbf{11a}^{\bullet} \rightarrow DCA + \mathbf{5a} \quad (18)$$

since this reaction should be exergonic by about −50 kcal/mol.[36] According to Scheme V, H-atom transfer from H-DCA$^{\bullet}$ to $\mathbf{11a}^{\bullet}$ competes with the trapping of $\mathbf{11a}^{\bullet}$ by $^3O_2$. Though electron-donor substituents stabilize cations much better than radicals,[37] radicals $\mathbf{11b}^{\bullet}$ and $\mathbf{11c}^{\bullet}$ should be somewhat better resonance stabilized than $\mathbf{11a}^{\bullet}$, obviously to an extent that allows these radicals and H-DCA$^{\bullet}$ to diffuse apart and subsequently react with $^3O_2$. This conclusion is drawn from the fact that at no stage of the photooxygenation of **2b** and **2c** did the ^1H NMR spectra of the reaction mixtures show the appearance of an aldehyde (**8**, **9b** and **9c**, respectively) as a result of the intermediate formation of **5b** and **5c** followed by oxygenation of these propenes according to Scheme III.

Substitution of one or two phenyl groups of **2a** by *p*-anisyl or *p*-phenoxyphenyl groups apparently stabilizes the radical cations $(\mathbf{2d–f})^{\bullet+}$ so efficiently that proton transfer cannot compete with dioxolane formation.[38] Thus, neither allylic hydroperoxides **4d–f** nor propenes **5d–f** and **6d–f** or their oxygenation products **7d–f**, **8**, **9d–f**, or **10** are formed.

Resonance stabilization of $\mathbf{Cp}^{\bullet+}$ ($\mathbf{2a}^{\bullet+} < \mathbf{2b}^{\bullet+} < \mathbf{2c}^{\bullet+} < \mathbf{2d}^{\bullet+} \approx \mathbf{2e}^{\bullet+} \approx \mathbf{2f}^{\bullet+}$) by $\Delta G \approx -4$ to −5 kcal/mol ($\mathbf{2a}^{\bullet+}$/$(\mathbf{2b,c})^{\bullet+}$) and −6.5 kcal/mol ($\mathbf{2a}^{\bullet+}$/$(\mathbf{2d–f})^{\bullet+}$), as inferred from the oxidation potentials of **2** (Table I), should result in an enhanced formation of free radical cations $Cp^{\bullet+}$ by shifting the equilibrium of $(DCA^{\bullet-}/Cp^{\bullet+})_{cage} \rightleftarrows DCA^{\bullet-} + Cp^{\bullet+}$ to the right hand side and thus in increased oxygenation rates as is shown in Table II.[39]

Conclusion

Oxygenation rates and product formation of 1,1-diaryl-2,2-diphenylcyclopropanes **2** in electron-transfer-induced oxygenation reactions photosensitized by DCA are governed by the resonance stabilization of the 1,3-radical cations $\mathbf{2}^{\bullet+}$. The increase of resonance stabilization of $\mathbf{2}^{\bullet+}$ is caused by substitution of one or two phenyl groups by electron-releasing aryl groups as is demonstrated by the concomitantly decreasing oxidation potential of the cyclopropane **2**. Enhanced resonance stabilization of $\mathbf{2}^{\bullet+}$ obviously favors the generation of free radical cations $\mathbf{2}^{\bullet+}$ by increasing the probability of radical ion pair ($DCA^{\bullet-}$/$\mathbf{2}^{\bullet+}$) separation, which, in turn, favors the dioxolane **3** formation by interaction of $\mathbf{2}^{\bullet+}$ with triplet ground-state oxygen. At the same time, enhanced resonance stabilization of $\mathbf{2}^{\bullet+}$ decreases the reactivity of $\mathbf{2}^{\bullet+}$ in proton transfer reactons with $DCA^{\bullet-}$ that yield allylic radicals $\mathbf{11}^{\bullet}$ and H-DCA$^{\bullet}$. Electron-donor substitution of free radicals $\mathbf{11}^{\bullet}$ apparently favors the drifting apart of $\mathbf{11}^{\bullet}$ and H-DCA$^{\bullet}$, thus increasing the probability of trapping of radical $\mathbf{11}^{\bullet}$

(34) To the best of our knowledge, dioxetanes, though often assumed to be the primary products of electron-transfer-induced oxygenations of olefins that lead to carbonyl cleavage products, have not yet been isolated. Dioxetanes, prepared by other methods, were shown to be cleaved to carbonyl compounds when exposed to DCA-sensitized photooxygenation conditions.[35]

(35) Foote, C. S. *Tetrahedron* **1985**, *41*, 2221.

(36) ΔG_{BDE}(C–H) = 22.3 kcal/mol for H–DCN$^{\bullet}$ → DCN + H$^{\bullet}$, ΔG_{BDE}(C–H) = 72 kcal/mol for **5a** → $\mathbf{11a}^{\bullet}$ + $^{\bullet}$H.[29] If ΔG_{BDE}(C–H) for the H-atom dissociation from H-DCA$^{\bullet}$ is approximately the same as that for H-DCN$^{\bullet}$ reaction 18 is exergonic by about −50 kcal/mol.

(37) Leigh, W. J.; Arnold, D. R.; Humphreys, R. W. R.; Wong, P. C. *Can. J. Chem.* **1980**, *58*, 2537 and references cited.

(38) Photosensitized rearrangement of **2d** to **5d** (and/or **6d**) could not be achieved in N_2-saturated MeCN in the presence of DCN. We suppose that this result is due to the decreased reactivity of $\mathbf{2d}^{\bullet+}$, as compared to $\mathbf{2a}^{\bullet+}$, which prevents the proton transfer to $DCN^{\bullet-}$. If a proton transfer would occur, the resulting radicals, $\mathbf{11d}^{\bullet}$ and H–DCN$^{\bullet}$, should be able, from an energetic point of view, to undergo an H-atom transfer to yield **5d** (and/or **6d**) + DCN as well as an electron transfer from $DCN^{\bullet-}$ to give $\mathbf{11d}^{-}$ + DCN. Though $\mathbf{11d}^{\bullet}$ should be somewhat more stable than $\mathbf{11a}^{\bullet}$, ΔG_{BDE}(C–H) for **5d** → $\mathbf{11d}^{\bullet}$ is certainly not much less than 70 kcal/mol so that an H-atom transfer should readily proceed. Furthermore, $E_{red}^{1/2}(\mathbf{11d}^{\bullet})$ may be more negative than −0.94 V (= $E_{red}^{1/2}(\mathbf{11a}^{\bullet})$) but hardly to such an extent that $DCN^{\bullet-}$ ($E_{red}^{1/2}(DCN)$ = −1.28 V) should not be able to transfer an electron to $\mathbf{11d}^{\bullet}$.

(39) The increase of the oxygenation rate is not due to an increased electron transfer between $^1DCA^*$ and Cp: the quenching rate constant k_q (Table I) increases from 1.06×10^{10} for **2a** to 1.48×10^{10} M^{-1} s^{-1} for **2f**, i.e., by a factor less than 1.5, whereas the time needed for the consumption of 1 molar equiv of O_2 is nearly 50 times longer for **2a** than for **2f**.

by $^3O_2$ to yield allylic hydroperoxide **4** and, concomitantly, decreasing the probability of a hydrogen atom transfer to produce the rearranged 1,1,3,3-tetraarylpropenes **5** and **6**.

Experimental Section

Solvents and commercially available compounds were purchased from standard suppliers and purified to match reported physical constants and spectral data. Special care was taken to obtain pure and dry MeCN; acetonitrile was therefore distilled over P_2O_5 and K_2CO_3 in sequence. 9,10-Dicyanoanthracene, mp 346–347 °C, was prepared according to the method of Beyer and Fritsch.[40] Other known compounds were prepared according to literature procedures and used (such as the 1,1-diarylethylenes **1a–f**) after appropriate purifications. Melting points are uncorrected.

UV spectra were recorded on a Zeiss RPQ 20C spectrometer. IR spectra were taken on a Bruker IFS 45 instrument either in Nujol or KBr or as thin films. ^1H NMR spectra were recorded on a Bruker WP-80 and a Varian XL 100 spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were recorded at 22.3 MHz on a Bruker WP-80 spectrometer with $CDCl_3$ as solvent and TMS as internal standard.

Fluorescence quenching of deoxygenated MeCN solutions of DCA (2×10^{-5} M) was executed on a Zeiss-4C fluorescence spectrometer equipped with a Xe lamp XBO 450 W. Excitation of DCA was carried out at 383 nm, and the fluorescence intensities were determined at 450 nm, i.e., at the first minimum of the DCA fluorescence spectrum. The quenchers, cyclopropanes **2a–f**, were used at at least six different concentrations between 0.002 and 0.030 M.

Redox potentials were measured by cyclic voltammetry on a cyclic voltammograph CV-1B (Bioanalytical Systems, Inc.) at a platinum electrode vs the standard calomel electrode (SCE) in Ar-saturated MeCN. The supporting electrolyte was tetraethylammonium tetrafluoroborate (0.1 M); scan speed 400 mV/s. The instrument was calibrated by using 1,3,5-trimethoxybenzene ($E_{ox}^{1/2} = 1.49$ V) as a standard.

Preparation of 1,1,2,2-Tetraarylcyclopropanes 2a–f. General Procedure. UV irradiations of 120 mL of dry benzene solutions containing between 0.40 and 0.05 mol of the respective 1,1-diarylethylenes **1a–f** and between 0.15 and 0.076 mol of 1,1-diphenyldiazomethane (DDM), prepared from benzophenone hydrazone,[41] were carried out in an immersion-type irradiation vessel equipped with a mercury high pressure lamp (Philips, HP 125 W) surrounded by a quartz water jacket. All reactions were run under dry nitrogen, and all solutions were purged with oxygen-free nitrogen for 15 min prior to the photochemical reaction. Irradiations, performed at 13 °C, lasted for about 15 to 30 h to obtain colorless solutions of the respective cyclopropanes. The workup procedure consisted of removal of benzene followed in some cases by chromatography of the oily product on acidic alumina (50-cm column) with various solvents and recrystallization of the colorless crystals from ethanol; in other cases, recrystallization from various solvents was sufficient to purify the cyclopropanes.

1,1,2,2-Tetraphenylcyclopropane (2a). 1,1-Diphenylethylene (**1a**) (72.0 g, 0.40 mol) and 29.1 g (0.15 mol) of DDM, irradiated for 30 h, gave 25.4 g of **2a** (colorless crystals, from ethanol/ethyl acetate; yield 48%), mp 167–168 °C (lit.[42] mp 167–168 °C). ^1H NMR: δ 2.50 (s, 2 H), 6.96 (m, 20 Ar H). UV (MeCN): λ_{max} = 230 nm (log ϵ = 4.23).

1-(4-Methylphenyl)-1,2,2-triphenylcyclopropane (2b). 1-(4-Methylphenyl)-1-phenylethylene (**1b**)[43] (14.6 g, 0.075 mol) and 14.6 g (0.076 mol) of DDM, irradiated for 18 h, afforded 12.7 g of **2b** (colorless crystals after chromatography on alumina, elution with toluene, and recrystallization from ethanol; yield: 47%), mp 143–144 °C. ^1H NMR: δ 2.18 (s, 3 H, CH_3), 2.48 (s, 2 H), 6.86–7.06 (m, 19 Ar H). ^{13}C NMR: δ 20.9 (q, CH_3), 25.2 (t, C-2), 43.8 and 44.0 (2 s, C-1, C-3). IR (KBr): 3055, 3022, 1599, 1514, 1493, 1445, 1321, 1008, 815, 777, 760, 725, 705, 695, 674, 631, 585, 534 cm^{-1}. UV (MeCN): λ_{max} = 235 nm (log ϵ = 4.31).

Anal. Calcd for $C_{28}H_{24}$ (360.47): C, 93.29; H, 6.71. Found: C, 93.21; H, 6.92.

1,1-Bis(4-methylphenyl)-2,2-diphenylcyclopropane (2c). 1,1-Bis(4-methylphenyl)ethylene (**1c**)[44] (15.6 g, 0.075 mol) and 14.6 g (0.076 mol) of DDM, irradiated for 20 h, gave 10.8 g of **2c** (colorless crystals from ethanol; yield: 38%), mp 131–132 °C. ^1H NMR: δ 2.15 (s, 6 H, 2 CH_3), 2.45 (s, 2 H), 6.80–6.98 (m, 18 Ar H). ^{13}C NMR: δ 20.9 (q, CH_3), 25.2 (t, C-2), 43.5 and 43.9 (2 s, C-1, C-3). IR (KBr): 3052, 3026, 2923, 1653, 1636, 1513, 1499, 734, 702, 693 cm^{-1}. UV (MeCN): λ_{max} = 225 nm (log ϵ = 4.39).

Anal. Calcd for $C_{29}H_{26}$ (374.50): C, 93.00; H, 7.00. Found: C, 93.30; H, 6.98.

1-(4-Methoxyphenyl)-1,2,2-triphenylcyclopropane (2d). 1-(4-Methoxyphenyl)-1-phenylethylene (**1d**)[45] (10.5 g, 0.050 mol) and 14.6 g (0.076 mol) of DDM, irradiated for 20 h, produced 9.8 g of **2d** (colorless crystals from ethanol/ethyl acetate; yield: 52%), mp 145–146 °C lit.[46] mp 145–146 °C). ^1H NMR: δ 2.46 (s, 2 H), 3.63 (s, 3 H, OCH_3), 6.96 (m, 19 Ar H). UV (MeCN): λ_{max} = 231 nm (log ϵ = 4.38).

1,1-Bis(4-methoxyphenyl)-2,2-diphenylcyclopropane (2e). 1,1-Bis(4-methoxyphenyl)ethylene (**1e**)[47] (12.0 g, 0.050 mol) and 14.6 g (0.076 mol) of DDM, irradiated for 15 h, yielded 10.6 g of **2e** (colorless crystals after chromatography on alumina, elution with CH_2Cl_2/toluene (3:7), and recrystallization from ethanol/ethyl acetate; yield: 52%), mp 107–108 °C (lit.[46] mp 107–108 °C). ^1H NMR: δ 2.31 (s, 2 H), 3.60 (s, 6 H, 2 OCH_3), 6.47–6.97 (m, 18 Ar H). UV (MeCN): λ_{max} = 228 nm (log ϵ = 4.39).

1,1-Bis(4-phenoxyphenyl)-2,2-diphenylcyclopropane (2f). 1,1-Bis(4-phenoxyphenyl)ethylene (**1f**)[48] (18.2 g, 0.050 mol) and 14.6 g (0.076 mol) of DDM, irradiated for 24 h, afforded 10.5 g of **2f** (colorless crystals from ethanol/ethyl acetate; yield: 69%), mp 139–140 °C. ^1H NMR: δ 2.48 (s, 2 H), 6.99 (m, 28 Ar H). ^{13}C NMR: δ 25.2 (t, C-2), 42.9 and 44.0 (2 s, C-1, C-3). IR (KBr): 3054, 3037, 1587, 1505, 1490, 1450, 1288, 1238, 1168, 873, 857, 755, 702, 692 cm^{-1}. UV (MeCN): λ_{max} = 240 nm (log ϵ = 4.53).

Anal. Calcd for $C_{39}H_{30}O_2$ (530.63): C, 88.27; H, 5.70. Found: C, 88.27; H, 5.64.

Photooxygenations and Photorearrangements of 1,1,2,2-Tetraarylcyclopropanes. Photooxygenations of 1,1,3,3-Tetraarylpropenes. General Procedure for Analytical and Kinetic Runs. A 25-mL irradiation unit with an automatic O_2 consumption recording system[19] was used for oxygen-uptake studies (O_2 uptake vs irradiation time) in the presence of various sensitizers and additives. Oxygen was bubbled through the solutions for 15 min before the irradiation cell was connected with the O_2-containing burette to obtain oxygen-saturated solutions. A mercury high pressure lamp HP 125 W (Philips) was used as a light source. A filter solution was placed between the lamp and the cell to cut off wavelengths shorter than 405 nm. The filter solution was prepared from 2.3 g of $CuSO_4 \cdot 5H_2O$, 3.0 g of $NaNO_2$, and 5 mL of concentrated ammonia diluted with distilled water to 100 mL.

The same irradiation cell, light source, and filter solution were applied for irradiations of deoxygenated solutions. No filter solution was applied when 1,4-dicyanonaphthalene (DCN) was used as a sensitizer. During the irradiations of deoxygenated solutions, the cell was disconnected from the oxygen burette and the recording system, and the solutions were saturated with oxygen-free nitrogen by passing N_2 through the solutions for 15 min before irradiations were commenced.

Samples were drawn from time to time and analyzed by their ^1H NMR spectra to determine the decrease of the starting cyclopropanes and to determine products and product distributions during irradiations of the O_2 as well as of the N_2-saturated solutions. The results are given in Tables II and III.

The ^1H NMR spectra of all the products are known: for 1,2-dioxolanes **3**, see below; for rearrangment products (1,1,3,3-tetraarylpropenes **5** and **6**), see ref 9; ketones and aldehydes were

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either purchased or prepared according to literature procedures.

Photooxygenation of 1,1,2,2-Tetraarylcyclopropanes. General Procedure for Preparative Runs. For preparative purposes, irradiations of 200 mL of oxygen-saturated MeCN solutions containing various amounts of the respective 1,1,2,2-tetraarylcyclopropane were carried out in an immersion-type irradiation vessel equipped with a mercury high pressure lamp (Philips, HP 125 W) surrounded by a glass water-jacket and another jacket of 1 cm width for a filter solution. The reactions were run in the presence of DCA (9.1 mg, 2×10^{-4} M) and under oxygen bubbling, which provided for a constant oxygen concentration and, at the same time, for vigorous stirring of the solution. A filter solution was applied, which was prepared from 5.6 g of $CuSO_4 \cdot 5H_2O$, 6.0 g of $NaNO_2$, and 10 mL of concentrated ammonia diluted with distilled water to 200 mL to cut-off wavelengths shorter than 405 nm. The reaction solutions were kept at 13 °C during the photooxygenation reactions. The progress of the reactions was followed by ^1H NMR analysis of samples drawn during the irradiations.

After more than 80% of the starting cyclopropane had disappeared, irradiations were finished and the solutions were worked up as described below.

3,3,5,5-Tetraphenyl-1,2-dioxolane (3a). 1,1,2,2-Tetraphenylcyclopropane (**2a**) (2.5 g, 7.2 mmol) was oxygenated in the presence of 1.1 g (7.2 mmol) of biphenyl within 25 h. After removal of MeCN, chromatography of the oily residue on alumina (50-cm column) with toluene, and recrystallization from ethanol, 0.68 g (yield: 25%) of **3a** was isolated; mp 178–179 °C (lit.[49] mp 178–179 °C). ^1H NMR: δ 4.05 (s, 2 H), 7.32 (m, 20 Ar H).

3-(4-Methylphenyl)-3,5,5-triphenyl-1,2-dioxolane (3b). 1-(4-Methylphenyl)-1,2,2-triphenylcyclopropane (**2b**) (2.5 g, 6.9 mmol) was oxygenated in the presence of 0.73 g (6.9 mmol) of $LiClO_4$ within 22 h. After removal of MeCN and recrystallization from ethanol, 0.78 g (yield: 29%) of **3b** was obtained; mp 129–130 °C. ^1H NMR: δ 2.25 (s, 3 H, CH_3), 4.06 (s, 2 H), 6.98–7.29 (m, 19 Ar H). ^{13}C NMR: δ 21.0 (q, CH_3), 62.3 (t, C-4), 92.5 (s, C-3, C-5). IR (KBr): 3058, 3024, 2922, 1600, 1492, 1447, 1015, 755, 698 cm^{-1}. UV (MeCN): λ_{max} = 255 nm (log ϵ = 3.85).

Anal. Calcd for $C_{28}H_{24}O_2$ (392.50): C, 85.68; H, 6.16. Found: C, 85.65; H, 6.15.

According to the ^1H NMR spectrum of the original product mixture, dioxolane **3b** and 4-methylbenzophenone (**7b**) were formed in a ratio of 7:3 (peak height ratio of the methyl protons).

3,3-Bis(4-methylphenyl)-5,5-diphenyl-1,2-dioxolane (3c). 1,1-Bis(4-methylphenyl)-2,2-diphenylcyclopropane (**2c**) (2.5 g, 6.7 mmol) afforded, after 15 h of irradiation, subsequent removal of MeCN, and recrystallization from ethanol, 1.9 g (yield: 70%) of **3c**; mp 127–128 °C (lit.[1c] mp 128 °C). ^1H NMR: δ 2.24 (s, 6 H, 2 CH_3), 4.03 (s, 2 H), 6.95–7.16 (m, 18 Ar H). ^{13}C NMR: δ 21.0 (q, CH_3), 62.3 (t, C-4), 92.4 and 92.5 (s, C-3, C-5). IR (KBr): 3061, 3025, 2921, 1510, 1493, 1449, 1016, 820, 699, 695 cm^{-1}. UV (MeCN): λ_{max} = 257 nm (log ϵ = 3.20).

4,4'-Dimethylbenzophenone (**7c**), mp 95 °C (lit.[50] mp 95 °C) was obtained as a minor product. According to the ^1H NMR spectrum of the original product mixture, dioxolane **3c** and ketone **7c** were formed in a ratio of 9:1 (peak height ratio of the methyl protons).

3-(4-Methoxyphenyl)-3,5,5-triphenyl-1,2-dioxolane (3d). 1-(4-Methoxyphenyl)-1,2,2-triphenylcyclopropane (**2d**) (2.5 g, 6.6 mmol) was quantitatively oxygenated within 1 h. After removal of MeCN and recrystallization from ethanol, 2.1 g (yield: 77%) of **3d** was isolated; mp 143–144 °C (lit.[1c] mp 142 °C). ^1H NMR: δ 3.70 (s, 3 H, OCH_3), 4.04 (s, 2 H), 6.65–7.29 (m, 19 Ar H). ^{13}C NMR: δ 55.2 (q, OCH_3), 62.5 (t, C-4), 92.4 and 92.6 (s, C-3, C-5). IR (KBr): 2926, 1608, 1512, 1491, 1447, 1244, 1180, 1020, 828, 756, 699 cm^{-1}. UV (MeCN): λ_{max} = 240 nm (log ϵ = 4.61).

3,3-Bis(4-methoxyphenyl)-5,5-diphenyl-1,2-dioxolane (3e). 1,1-Bis(4-methoxyphenyl)-2,2-diphenylcyclopropane (**2e**) (2.5 g, 6.1 mmol) was quantitatively oxygenated in less than 1 h. After removal of MeCN and recrystallization from *n*-hexane and finally from ethanol, 2.1 g (yield: 79%) of **3e** was obtained; mp 107–108 °C (lit.[1c] mp 106 °C). ^1H NMR: δ 3.61 (s, 6 H, 2 OCH_3), 3.99 (s, 2 H), 6.62–7.24 (m, 18 Ar H). ^{13}C NMR: δ 55.2 (q, OCH_3), 62.7 (t, C-4), 92.3 and 92.7 (s, C-3, C-5). IR (KBr): 1610, 1512, 1251, 1177, 1029, 828, 704 cm^{-1}. UV (MeCN): λ_{max} = 273 nm (log ϵ = 4.08).

3,3-Bis(4-phenoxyphenyl)-5,5-diphenyl-1,2-dioxolane (3f). 1,1-Bis(4-phenoxyphenyl)-2,2-diphenylcyclopropane (**2f**) (2.0 g, 3.8 mmol) was quantitatively oxygenated within 1 h. After removal of MeCN and recrystallization from ethanol, 1.3 g (yield: 61%) of **3f** was isolated; mp 123–124 °C. ^1H NMR: δ 4.00 (s, 2 H), 6.75–7.29 (m, 28 Ar H). ^{13}C NMR: δ 62.6 (t, C-4), 92.1 and 92.6 (s, C-3, C-5). IR (KBr): 3061, 1588, 1505, 1489, 1240, 871, 751, 693 cm^{-1}. UV (MeCN): λ_{max} = 232 nm (log ϵ = 4.48).

Anal. Calcd for $C_{39}H_{30}O_4$ (562.67): C, 83.25; H, 5.37. Found: C, 83.34; H, 5.27.

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