

Substituent-Dependent Electron-Transfer Induced Photooxygenation of 1,1-Diarylethylenes

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Rates and products of 9,10-dicyanoanthracene-sensitized photooxygenations of 1,1-diarylethylenes (1a-r) in acetonitrile were studied. If at least one of the aryl groups carries an electron-donating substituent at the *para* (or *ortho*) position (1a-1), 3,3,6,6-tetraaryl-1,2-dioxanes (2a-1) are generated in high yields (85-100%). Benzophenones (3) are the only other observable products. 1,1-Diphenylethylene (1n) and its *m*-methoxy (1m), *p*-chloro (1o,p), and *p*-nitro (1q,r) derivatives, however, yield mainly benzophenones (3m-r) (>50%) (the *p*-nitro compounds only in the presence of biphenyl). 1,2-Dioxanes (2m-p), cyclobutanes (4n-p), and α -tetralones (5m-o) are obtained as side products. Dioxanes, benzophenones, and α -tetralones are products of electron-transfer induced oxygenations involving triplet ground-state molecular oxygen, $^3\text{O}_2$. Singlet molecular oxygen, $\text{O}_2(^1\Delta_g)$, contributes to the benzophenone formation from strongly electron-donor substituted diarylethylenes. An exception is the most powerful electron-donor substituted diarylethylene 1a, with which $\text{O}_2(^1\Delta_g)$ undergoes an electron-transfer reaction affording dioxane 2a. Dioxane formation proceeds via free-radical cations $1^{+\cdot}$, which enter into a chain reaction with 1, $^3\text{O}_2$, and another molecule of 1 to yield dioxane 2 and a new radical cation $1^{+\cdot}$ that maintains the chain reaction. The efficiency of this chain process, however, is found to be several orders of magnitude smaller than expected. To explain this result, a 1,6-biradical $^1\text{1-1-O}_2^{\cdot}$ is proposed to be generated in this chain reaction as the product-determining intermediate that predominantly fragments into $^3\text{O}_2$ and two molecules of 1. Cyclization to dioxane 2 and transformation to benzophenone 3 occur at presumably less than 0.1% from this biradical. The pathways leading to cyclobutanes (4) and α -tetralones (5) are also discussed.

Introduction

Oxidation of 1,1-diphenylethylene (1n) by molecular oxygen has been carried out under various conditions. Autoxidation was reported to yield a polymeric peroxide.^{1,2} Low-temperature oxidations in Lewis-acidic solvents such as SO_2 gave rise to the formation of benzophenone (3n) in low yields.³ Photosensitization by dyes such as methylene blue yielded 3n⁴ whereas that by benzil⁵ or 9,10-dicyanoanthracene (DCA)⁶ afforded a mixture of 3n and 1,1-diphenyloxirane. 3,3,6,6-Tetraphenyl-1,2-dioxane (2n) was obtained as the main product (80%), when the CT-complex of 1n with SbCl_5 was irradiated in CH_2Cl_2 at -78°C .⁷ More recently, DCA-photosensitized oxygenation of 1n in acetonitrile (MeCN) at room temperature was shown to yield mainly 2n and 3n in a ratio of about 1:2.^{8,9}

When donor-substituted 1,1-diarylethylenes such as 1,1-bis(4-methoxyphenyl)ethylene (1b) were used, the corresponding 1,2-dioxanes, e.g., 2b, were obtained in almost quantitative yields by photosensitization with cyanoaromatics in MeCN.⁸⁻¹⁰ However, only 4,4'-dimethoxybenzophenone (3b) was observed when the oxygenation of 1b was photosensitized by DCA in CH_2Cl_2 ¹¹ or by rose bengal in MeCN.¹²

Formation of dioxane 2 was shown to be induced by electron transfer from ethylene 1 to SbCl_5 in the electronically excited CT-complex of (1- SbCl_5) or from 1 to singlet excited DCA ($^1\text{DCA}^*$) during an encounter in a polar solvent. Addition of ethylene 1 to $1^{+\cdot}$, present either in a complex with SbCl_5^- or as a solvated free-radical cation, followed by addition of $^3\text{O}_2$ gives radical cation $(1-1-\text{O}_2)^{+\cdot}$ that is reduced to dioxane 2 either by SbCl_5^- in a nonchain reaction⁷ or by ethylene 1 in a chain reaction.⁸⁻¹⁰

The mechanism of ketone (3) production during DCA-photosensitized oxygenations is not yet established. Formation of 3n via an unstable dioxetane, generated by reaction of $1n^{+\cdot}$ with either superoxide $\text{O}_2^{\cdot-}$, as was originally proposed,⁶ or $^3\text{O}_2$ seems to be rather unlikely. Reaction of $^3\text{O}_2$ with $(1n-1n)^{+\cdot}$ is considered as a more likely pathway that leads to 3n in competition with that yielding dioxane 2n.⁹

Ketone 3b is obviously formed by interaction of singlet oxygen, $\text{O}_2(^1\Delta_g)$, with the electron-rich diarylethylene 1b.¹² The occurrence of this pathway is corroborated by the observation that the product ratio, dioxane 2b/ketone 3b, depends on the sensitizer used.¹³

In order to learn more about the substituent-dependent electron-transfer photooxygenation of 1,1-disubstituted ethylenes, we studied a series of 1,1-diarylethylenes (1a-r), the oxidation potentials of which vary from 0.66 V for the most powerful electron-donor substituted 1,1-bis[4-

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(1) Staudinger, H. *Ber. Dtsch. Chem. Ges.* 1925, 58, 1075.

(2) Kropf, H.; Gürtler, D. *Liebigs Ann. Chem.* 1976, 519.

(3) Nagai, T.; Miyazaki, T.; Sonoyama, Y.; Tokura, N. *J. Polym. Sci., Polym. Chem. Educ.* 1968, 6, 3087.

(4) Rio, G.; Berthelot, J. *Bull. Soc. Chim. Fr.* 1969, 3609.

(5) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* 1976, 98, 4193.

(6) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* 1980, 102, 6083.

(7) Haynes, R. K.; Probert, M. K. S.; Wilmot, I. D. *Aust. J. Chem.* 1978, 31, 1737.

(8) Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* 1984, 25, 2735.

(9) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* 1986, 108, 7356.

(10) Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* 1984, 25, 185.

(11) Schaap, A. P.; Zaklika, K. A.; Kaskar, B.; Fung, L. W.-M. *J. Am. Chem. Soc.* 1980, 102, 389.

(12) Gollnick, K.; Held, S. *J. Photochem. Photobiol., A: Chem.* 1991, 59, 55. Erratum: *Ibid.* 1992, 63, 379.

(13) Gollnick, K.; Held, S. *J. Photochem. Photobiol., A: Chem.* 1993, 70, 135.

(14) Rehm, D.; Weller, A. *Isr. J. Chem.* 1970, 8, 259.

Table I. DCA-Photosensitized Oxygenation of 1,1-Diarylethylenes (1) in Acetonitrile: Oxidation Potentials, $E_{ox}(1)$, Rate Constants of DCA-Fluorescence Quenching, k_q , Yields of 1,2-Dioxanes 2 and Ketones 3, and Oxidation Potentials of 1,2-Dioxanes, $E_{ox}(2)$

1	R ^a in		$E_{ox}(1)^b$ (V)	k_q ($10^{10} \text{ M}^{-1} \text{ s}^{-1}$) k_{et}^c ($10^{10} \text{ M}^{-1} \text{ s}^{-1}$)		2 (%)	3 (%)	$E_{ox}(2)^d$ (V)	$\Delta G'^e$ (eV)
	Ar ₁	Ar ₂		expl	calcd				
a	4-N(Me) ₂	4-N(Me) ₂	0.66	f	1.50	100	—	f	
b	4-OMe	4-OMe	1.32	1.84	1.39	97	3	1.66	-0.34
c	4-OMe	4-Me	1.38	1.64	1.37	95	5	1.66	-0.28
d	4-OMe	— ^g	1.39	1.73	1.36	100	—	1.81	-0.42
e	4-OMe	4-Cl	1.44	1.54	1.34	90	10	1.82	-0.38
f	2-OMe	2-OMe	1.46	1.69	1.33	90	10	1.72	-0.26
g	4-OMe	4-NO ₂	1.53	f	1.29	90	10	1.81	-0.28
h	4-OPh	4-OPh	1.54	1.40	1.29	97	3	1.84	-0.30
i	4-Me	4-Me	1.66	1.35	1.18	90	10	>2	<-0.34
j	4-CD ₃	4-CD ₃	1.66	1.39	1.18	90	10	>2	<-0.34
k	4-Me	—	1.75	1.24	1.06	85	15	>2	<-0.25
l	2,4-Me ^h	—	1.79	1.09	0.98	85	15	>2	<-0.21
m	3-OMe	3-OMe	1.75	1.39	1.06	<5	50 ^j	>2	<-0.25
n	—	—	1.88	0.87	0.74	30	50 ^j	>2	<-0.12
o	4-Cl	—	1.89	0.68	0.70	25	50 ^j	>2	<-0.11
p	4-Cl	4-Cl	1.90	0.73	0.67	20	70 ^k	>2	<-0.10
q	4-NO ₂	—	>2	f	0.21	—	80 ^l	>2	
r	4-NO ₂	4-NO ₂	>2	f		—	20 ^l		

^a Ar₁ = Ar₂ = RC₆H₄. ^b Irreversible oxidation potentials of ethylenes 1 in MeCN (*vs* SCE). ^c k_{et} calcd by employing the Rehm-Weller equation¹⁴ $k_{et} = (2 \times 10^{10}) [1 + 0.25 \{ \exp(\Delta G^\ddagger/RT) + \exp(\Delta G/RT) \}]^{-1} \text{ M}^{-1} \text{ s}^{-1}$ in MeCN (20 °C), with $\Delta G = 23.06 [E_{ox}(1) - E_{red}^{1/2}(\text{DCA}) - e_o^2/er - E_{o,o}(\text{DCA})] \text{ kcal mol}^{-1}$, using $e_o^2/er = 0.06 \text{ eV}$, $E_{red}^{1/2}(\text{DCA}) = -0.89 \text{ V}$, and $E_{o,o}(\text{DCA}) = 2.88 \text{ eV}$, and with $\Delta G^\ddagger = \Delta G/2 + [(\Delta G/2)^2 + (\Delta G^\ddagger(0))^2]^{1/2}$ and $\Delta G^\ddagger(0) = 2.4 \text{ kcal mol}^{-1}$. ^d Irreversible oxidation potentials of 1,2-dioxanes 2 in MeCN (*vs* SCE). ^e $\Delta G' = E_{ox}(1) - E_{ox}(2)$. ^f Not determined. ^g — indicates R = H; i.e., Ar = C₆H₅. ^h Ar₁ = R, RC₆H₃. ⁱ +25% of the corresponding α -tetralone derivative. ^j +10% of the corresponding cyclobutane derivative and 10% of the corresponding α -tetralone derivative. ^k +10% of the corresponding cyclobutane derivative. ^l After addition of 0.025 M of biphenyl.

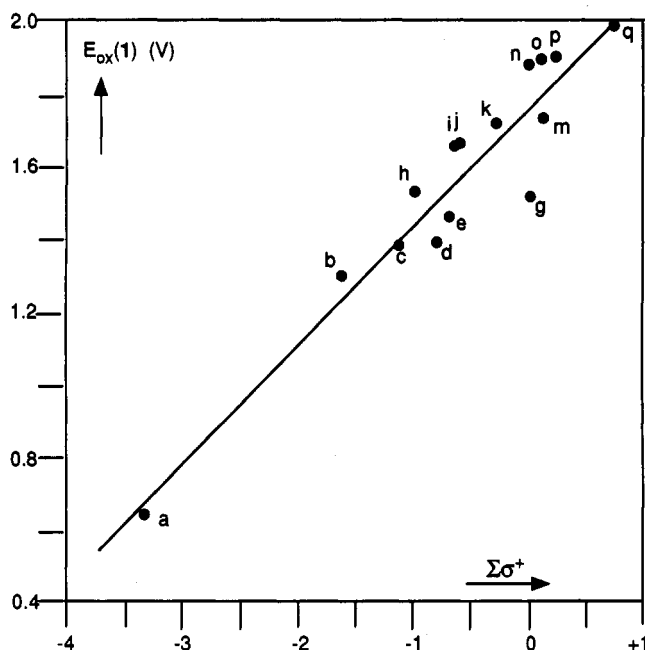


Figure 1. Plot of oxidation potentials $E_{ox}(1)$ vs $\Sigma\sigma^+$ of para- and meta-substituted 1,1-diarylethylenes 1.

(*N*-dimethylamino)phenyl]ethylene (1a) to over 2 V for the most powerful electron-acceptor substituted 1,1-bis(4-nitrophenyl)ethylene (1r).

Results

Oxidation Potentials of and DCA Fluorescence Quenching by 1,1-Diarylethylenes. The (irreversible) oxidation potentials $E_{ox}(1)$ of 1,1-diarylethylenes 1a–r, prepared as described in the Experimental Section, depend on the nature, number, and position of the substituents of the aryl groups (Table I).

Figure 1 shows that $E_{ox}(1)$ is linearly related to the sum of the σ^+ -values of para- and meta-substituents. Equation

1 was obtained by using the σ^+ -values reported by Brown and Okamoto¹⁵ and applying a regression analysis (correlation factor $r = 0.963$).

$$E_{ox}(1) = 0.32\Sigma\sigma^+ + 1.78 \text{ (V)} \quad (1)$$

The experimental values of $E_{ox}(1)$ deviate from those calculated by no more than $\pm 0.10 \text{ V}$, except for 1g where the deviation is -0.2 V . Diarylethylene 1g, however, represents a strongly donor–acceptor substituted derivative, and its easy oxidation may be attributed to mero-stabilization of $1g^{+\cdot}$.¹⁶

Oxidation potentials $E_{ox}(2)$ of 3,3,6,6-tetraaryl-1,2-dioxanes 2a–p were also determined and found to be always larger than those of the corresponding 1,1-diarylethylenes from which they were formed.

DCA-fluorescence is efficiently quenched by diarylethylenes 1 in deoxygenated MeCN solution. Fluorescence quenching constants k_q were determined from the slopes ($k_q\tau_1$) of Stern–Volmer plots by using $\tau_1 = 15.3 \text{ ns}$ ¹⁷ as the lifetime of ¹DCA* in MeCN. The good agreement between k_q and the electron-transfer constants k_{et} obtained from the Rehm–Weller equations¹⁴ (Table I) supports the view that fluorescence quenching is caused by electron transfer.

DCA-Photosensitized Oxygenation of 1,1-Diarylethylenes in MeCN. Photooxygenation Products. Donor-substituted 1,1-diarylethylenes 1a–l yield 1,2-dioxanes 2a–l as major products ($\geq 85\%$) and benzophenones 3a–l as minor products (<5% from 3a–d and 3h; 10–15% from 3e–g and 3i–l; see Table I).

1,1-Diphenylethylene (1n) and its *p*-chloro-substituted derivatives 1o and 1p, however, afford mainly benzophenones 3n–p ($\geq 50\%$). 1,2-Dioxanes 2n–p (20–30%), cyclobutanes 4n–p ($\sim 10\%$), as well as α -tetralones 5n and 5o + 5o' ($\sim 10\%$) are produced as additional products.

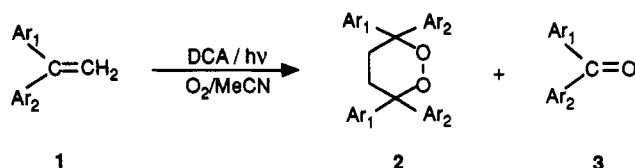
(15) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* 1958, 80, 4979.

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

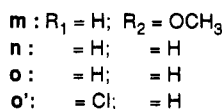
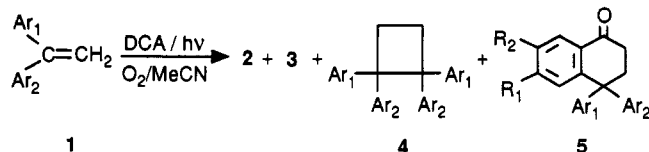
(17) Manring, L. E.; Gu, C. I.; Foote, C. S. *J. Phys. Chem.* 1983, 87, 40.

(18) Gollnick, K.; Schnatterer, A. *Photochem. Photobiol.* 1986, 43, 365.

**Scheme I. 1,2-Dioxanes (2) and Ketones (3)
Obtained from 1,1-Diarylethylenes 1a-1l**



**Scheme II. 1,2-Dioxanes (2), Ketones (3),
Cyclobutanes (4), and α -Tetralones (5) Obtained
from 1,1-Diarylethylenes 1m-1r**



Similarly, the *m,m'*-dimethoxy-substituted diphenylethylene **1m** gives rise to 50% of benzophenone **3m** and about 25% of α -tetralone **5m** but to less than 5% of 1,2-dioxane **2m**. With very slow rates, and only in the presence of some biphenyl as a cosensitizer, the strongly acceptor-substituted diarylethylenes **1q** and **1r** yield benzophenones **3q** and **3r** as the only identifiable products.

Photooxygenation Rates. Initial photooxygenation rates ν_0 were determined for oxygen-saturated MeCN solutions of 0.025 M of **1**. The presence of 0.025 M of lithium perchlorate (LP) increases the initial rates of O₂ consumption to ν_L (Table II). With electron-donor substituted diarylethylenes such as **1b** and **1i**, ketone formation decreases remarkably in the presence of LP. With 1,1-diphenylethylene (**1n**), only dioxane **2n** and ketone **3n** were identified with certainty, but other (unidentified) products were also formed, and some **2n** is apparently decomposed in the presence of LP.

Rate enhancement, due to the "special salt effect" exerted by LP, is relatively large for the *p,p'*-dimethoxy derivative **1b**, appreciable for the other *p*-methoxy-substituted 1,1-diphenylethylenes **1c-e** and **1g** as well as for the *p,p'*-diphenoxy compound **1h**, moderate for the *o,o'*-dimethoxy derivative **1f** and for the methyl-substituted 1,1-diphenylethylenes **1i-l**, and rather small (but not negligible) for diphenylethylene **1n**, its *m,m'*-dimethoxy derivative **1m** and its *p*-chloro derivatives **1o** and **1p**.

We have recently used the "special salt effect" to determine the efficiencies α_0 with which solvent-separated radical ion pairs (SSIP) dissociate into solvated free-radical ions (SFRI). We found that, in O₂-saturated MeCN, (DCA⁻/1b^{•+})_{SSIP} dissociates into (DCA⁻)_s and (1b^{•+})_s with an efficiency $\alpha_{0(1b)} = 0.38$ and that (1b^{•+})_s yielded dioxane **2b** with an efficiency $\eta_{0(1b)} = 4.1$.¹⁹ By using $\alpha_{0(1b)}\eta_{0(1b)} = 1.56$, the values of $\alpha_0\eta_0$ for the other 1,1-diarylethylenes shown in Table II are estimated.

By ferrioxalate actinometry, Eriksen and Foote⁶ determined a quantum yield of 0.8 for the disappearance of **1n** (at "infinite" concentration) in O₂-saturated MeCN in the presence of DCA and light ($\lambda_{exc} = 405$ nm). If this value is used as a reference, the $\alpha_0\eta_0$ values are larger than

Table II. DCA-Photosensitized Oxygenation of 0.025 M Solutions of 1,1-Diarylethylenes (1) in Acetonitrile: Total Oxygen Consumption (O_{2,tot}), Initial Oxygen Consumption Rates in the Absence (ν_0) and Presence of LiClO₄ (ν_L), Initial Quantum Yields of Solvent-Separated Radical Ion Pair Formation (Φ_{SSIP}), $\alpha_0\eta_0$ Values, and Values of ΔG_{back} Associated with Back-Electron Transfer within the SSIPs

1	[LiClO ₄] (M)	O _{2,tot} (mol equiv)	ν^a (mL h ⁻¹)	ν_L/ν_0^b	Φ_{SSIP}^c	$\alpha_0\eta_0^d$	ΔG_{back}^e (eV)
a		0.5	19.9	<i>f</i>	0.77	<i>f</i>	-1.55
	0.025		49.5				
b		0.5	48.2	10.7	0.80	1.6	-2.21
	0.025		510.6				
c		0.5	66.4	5.1	0.78	2.2	-2.27
	0.025		340.3				
d		0.5	91.3	4.7	0.79	3.0	-2.28
	0.025		422.5				
e		0.5	38.5	4.6	0.77	1.3	-2.33
	0.025		180.9				
f		0.5	23.1	1.5	0.79	0.8	-2.35
	0.025		35.1				
g		0.5	42.6	4.2	0.74	1.5	-2.43
	0.025		181.5				
h		0.5	86.7	5.9	0.75	3.0	-2.43
	0.025		510.5				
i		0.5	74.9	1.4	0.75	2.6	-2.55
	0.025		108.4				
j		0.5	67.5	1.5	0.75	2.3	-2.55
	0.025		101.3				
k		0.6	40.6	1.4	0.73	1.4	-2.64
	0.025		57.0				
l		0.6	56.1	1.4	0.71	2.0	-2.68
	0.025		77.8				
m		0.8	11.4	1.1	0.75	0.4	-2.64
	0.025		12.9				
n		0.8	21.2	1.1	0.66	0.8	-2.77
	0.025		22.5				
o		0.8	15.9	1.1	0.60	0.7	-2.78
	0.025		17.0				
p		0.9	9.1	1.1	0.62	0.4	-2.79
	0.025		10.2				

^a ν determined at [1] = 0.025 M. ^b $\nu_0 = \nu$ at [LiClO₄] = 0; $\nu_L = \nu$ at [LiClO₄] = 0.025 M. ^c Calculated by using eq 3, with k_q taken from Table I, $\tau_1 = 15.3$ ns,¹⁷ $k_o[O_2] = 4.86 \times 10^7$ s⁻¹,¹⁸ and [1] = 0.025 M. ^d $\alpha_0\eta_0 = \nu_0/(I_A\Phi_{SSIP})$, with $I_A = \nu_{0(1b)}/(\Phi_{SSIP(1b)}\alpha_{0(1b)}\eta_{0(1b)}) = 38.67$ mL h⁻¹, since $\alpha_{0(1b)} = 0.38$ and $\eta_{0(1b)} = 4.1$.¹⁹ ^e $\Delta G_{back} = E_{red}^{1/2}(DCA) - E_{ox}(1)$. ^f Not determined; see text.

those shown in Table II by a factor of 1.55 for compounds **1b-j** and 1.28 for **1k** and **1l** but smaller by a factor of 0.75 for **1p**.

Discussion

1,2-Dioxane Formation. 1,2-Dioxanes are generated in a chain reaction involving triplet ground-state oxygen, ³O₂.⁸⁻¹⁰ Scheme III shows the reactions involved in 1^{•+} formation and the minimum number of steps leading from radical cation 1^{•+} to 1,2-dioxane **2**.

According to this scheme, the rate of O₂ consumption is given by eq 2 in which I_A is the number of light quanta

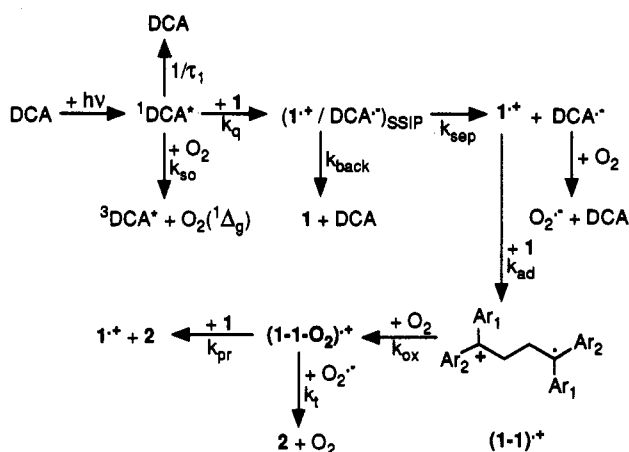
$$\nu_0 = I_A\Phi_{ox} = I_A\Phi_{SSIP}\alpha_0\eta_0 \quad (2)$$

absorbed by DCA per unit of time (for convenience converted into "mL light quanta per hour"), Φ_{ox} and Φ_{SSIP} are the quantum yields of oxygenation and SSIP formation, α_0 is the efficiency with which SFRI are formed from SSIP, and η_0 represents the efficiency with which the radical cation 1^{•+} undergoes the chain reaction that yields the 1,2-dioxane **2**.

In particular, the reaction is induced by an electron transfer from 1,1-diarylethylene **1** to singlet excited DCA, ¹DCA*, generating (1^{•+}/DCA⁻)_{SSIP} with a quantum yield Φ_{SSIP} given by eq 3 in which k_q is the rate constant of DCA-fluorescence quenching assumed to be equal to the

(19) Gollnick, K.; Wellenhofer, G. *J. Photochem. Photobiol., A: Chem.*, in press.

**Scheme III. 3,3,6,6-Tetraaryl-1,2-dioxane (2)
Formation by Electron-Transfer Oxygenation of
1,1-Diarylethylenes (1) Photoinduced by DCA in
Acetonitrile**



$$\Phi_{\text{SSIP}} = k_q[1]/(1/\tau_1 + k_q[1] + k_{\text{so}}[\text{O}_2]) \quad (3)$$

rate constant of electron transfer that yields $(1^{\bullet+}/\text{DCA}^{\bullet-})_{\text{SSIP}}$, k_{so} is the rate constant of $^1\text{DCA}^*$ -quenching by $^3\text{O}_2$, and τ_1 is the lifetime of $^1\text{DCA}^*$ in O_2 -free MeCN solution.

In competition with back-electron transfer, the SSIP separates into SFRI, $(1^{\bullet+})_s + (\text{DCA}^{\bullet-})_s$, with an efficiency α_0 defined by eq 4 in which k_{sep} and k_{back} represent the

$$\alpha_0 = k_{\text{sep}}/(k_{\text{sep}} + k_{\text{back}}) \quad (4)$$

rate constants of SFRI formation from and back-electron transfer within the SSIP, respectively.

Addition of $1^{\bullet+}$ to 1 to yield $(1-1)^{\bullet+}$ may be expected to increase with increasing nucleophilicity of the olefinic partner 1. If the rate of addition of $1n^{\bullet+}$ to 1n is almost diffusion-controlled as reported ($k_{\text{ad}} \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$),⁹ those of $(1b-1)^{\bullet+}$ to the corresponding diarylethylenes 1 may be only slightly faster until they reach the limiting value of $k_{\text{ad}} (= k_{\text{dif}} = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$.

Since addition of $^3\text{O}_2$ to 1,2-radical cations is generally rather slow, addition of $^3\text{O}_2$ to $1^{\bullet+}$ cannot compete with that of $1^{\bullet+}$ to diarylethylene 1.⁹ On the other hand, $^3\text{O}_2$ -addition to the 1,4-radical cation $(1-1)^{\bullet+}$ to give $(1-1-\text{O}_2)^{\bullet+}$ may be assumed to occur with an almost diffusion-controlled rate ($k_{\text{ox}} \approx k_{\text{dif}}$), since the radical site in $(1-1)^{\bullet+}$, separated from the cationic site by two isolating CH_2 groups, should be as reactive toward $^3\text{O}_2$ as an aliphatic (mono)radical.

The resultant 1,6-radical cation $(1-1-\text{O}_2)^{\bullet+}$ is expected to be reduced to the 1,2-dioxane 2 by two competing reactions: (1) by the chain-propagating interaction with 1 (k_{pr}) and (2) by the chain-terminating reaction with superoxide, $\text{O}_2^{\bullet-}$ (k_t). Both steps should proceed with almost diffusion-controlled rates since the secondary electron transfer from 1 to $(1-1-\text{O}_2)^{\bullet+}$ is associated with $\Delta G'$ values between about -0.3 and -0.4 eV (Table I) and that of $\text{O}_2^{\bullet-}$ to $(1-1-\text{O}_2)^{\bullet+}$ with $\Delta G''$ values of ≤ -2.44 eV ($\Delta G'' = E_{\text{red}}(\text{O}_2) - E_{\text{ox}}(2)$).²⁰

(20) Chain termination will take place by $\text{O}_2^{\bullet-}$ rather than by $\text{DCA}^{\bullet-}$. Radical anion $\text{DCA}^{\bullet-}$ ($E_{\text{red}}^{1/2}(\text{DCA}) = -0.89 \text{ V}^{21}$) is trapped by $^3\text{O}_2$ ($E_{\text{red}}^{1/2}(\text{O}_2) = -0.78 \text{ V}^{21}$) in an exothermic electron transfer reaction occurring with an almost diffusion-controlled rate²² before it can deliver its extra electron to $(1-1-\text{O}_2)^{\bullet+}$, since the oxygen concentration is several orders of magnitude larger than that of the radical cation.

Provided that no other reactions occur than those shown in Scheme III, the efficiency η_0 equals the chain length n , given by eq 5, with which dioxane 2 is generated from radical cation $1^{\bullet+}$.

$$n = k_{\text{pr}}[1]/k_t[\text{O}_2^{\bullet-}] \approx [1]/[\text{O}_2^{\bullet-}] \quad (5)$$

Under the reaction conditions used in this study, the concentration of 1 is always several orders of magnitude larger than that of $\text{O}_2^{\bullet-}$, and thus η_0 is expected to be very large.

As long as one of the aryl groups bears an electron-donor substituent at the *para* or *ortho* position, the DCA-photosensitized oxygenation of 1,1-diarylethylenes (1a-1) yields mainly 3,3,6,6-tetraaryl-1,2-dioxanes (2a-1). From unsymmetrically substituted 1,1-diarylethylenes, mixtures of *cis-trans* isomers of the corresponding dioxanes are obtained.

When one of the aryl groups of 1 carries a rather powerful electron-donor, e.g., a *p*-methoxy group as in 1b-e and 1g, the yield of the corresponding dioxane 2 is only slightly influenced by the electron-donating or electron-accepting properties of the substituents of the second aryl group. However, there seems to be a rather peculiar, though not large, influence on the oxygenation rates and thus on the values of $\alpha_0\eta_0$. Relative to the *p*-anisylphenyl derivative 1d, the O_2 -uptake rates ν_0 and the values of $\alpha_0\eta_0$ decrease with increasing electron-donor properties of the substituents of the second aryl group (1d > 1c > 1b) as well as with increasing electron-acceptor properties (1d > 1e \approx 1g).

We have recently shown that the efficiency α_0 of free-radical ion formation from SSIP increases from 0.38 for 1b to 0.65 for 1i to 0.8 for 1n, while the efficiency η_0 with which the corresponding radical cations $1^{\bullet+}$ yield dioxanes decreases from 4.1 to 3.6 to 0.7 for these compounds.¹⁹

Within the limits of error, $k_{\text{sep}} (= (8 \pm 2) \times 10^7 \text{ s}^{-1})$ was found to be independent of the nature of $1^{\bullet+}$, whereas $k_{\text{back}} (= 1.6 \times 10^8, 3.4 \times 10^7, \text{ and } 2 \times 10^7 \text{ s}^{-1}$ for 1b, 1i, and 1n, respectively) increased with decreasing oxidation potential of the 1,1-diarylethylene 1, i.e., with decreasing energy content of the SSIP in the range from about -2 to -3 eV, the so-called "Marcus inverted region".¹⁹ Experimental evidence for such a behavior of the back-electron transfer in the "Marcus inverted region"²³ has been gathered during the last years by several research groups.²⁴

We may therefore conclude that the efficiency α_0 of free-radical ion formation increases from about 0.4 for 1b to about 0.7 for 1l and that the efficiency η_0 with which radical cations $(1b-1)^{\bullet+}$ yield dioxanes 2b-1 varies between ~ 1 (for 1f) and 7 (for 1d).

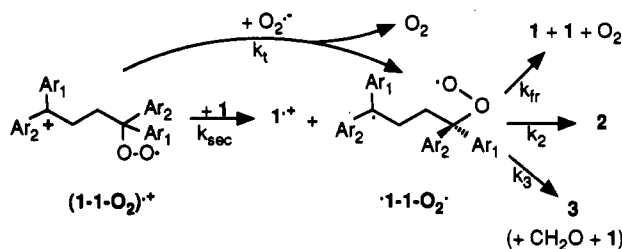
(21) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233.

(22) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* 1980, 102, 391.

(23) (a) Marcus, R. A. *J. Chem. Phys.* 1956, 24, 966. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* 1964, 15, 155.

(24) (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* 1984, 106, 5057. (b) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* 1985, 107, 1080. (c) Irvine, M. P.; Harrison, R. J.; Beddard, G. S.; Leighton, P.; Sanders, J. K. M. *Chem. Phys.* 1986, 104, 315. (d) Ohno, T.; Yoshimura, A.; Mataga, N. *J. Phys. Chem.* 1986, 90, 3295. (e) Closs, G. L.; Miller, J. R. *Science* 1988, 240, 440. (f) Vauthey, E.; Suppan, P.; Haselbach, E. *Helv. Chim. Acta* 1988, 71, 93. (g) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* 1987, 109, 3794. (h) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. *J. Am. Chem. Soc.* 1988, 110, 1991. (i) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* 1988, 110, 7242. (j) Gould, I. R.; Moser, J. E.; Armitage, B.; Farid, S.; Goodman, L. L.; Herman, M. S. *J. Am. Chem. Soc.* 1989, 111, 1917. (k) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* 1990, 112, 4290. (l) Kikuchi, K.; Takahashi, Y.; Hoshi, M.; Niwa, T.; Katagiri, T.; Miyashi, T. *J. Phys. Chem.* 1991, 95, 2378.

Scheme IV. Proposed Extension of the Mechanism Shown in Scheme III To Explain Large Chain Lengths and Low Efficiencies of Formation of 1,2-Dioxanes 2 (η_o) and Ketones 3 ($\eta_{(3)}$)



Obviously, the η_o values thus obtained are several orders of magnitude smaller than expected (see above). This result indicates that at least one very efficient energy-wasting reaction has to be added to the reactions shown in Scheme III.

We propose that the reduction of the radical cation (1-1-O₂)^{•+} not only yields dioxane 2 but also restores the educts 1 and molecular oxygen via a common 1,6-biradical [•]1-1-O₂[•] (Scheme IV).

The intermediate [•]1-1-O₂[•], generated by a secondary electron transfer from 1 to (1-1-O₂)^{•+} with a rate constant k_{sec} ($\approx k_{diff}$), either undergoes a fragmentation into triplet ground-state oxygen, ³O₂, and two molecules of 1 (k_{fr}) or cyclizes to a dioxane 2 (k_2) (if, at this point, we disregard ketone 3 formation which will be discussed in the following paragraph). Dioxane 2 is thus formed from 1^{•+} with an efficiency η_o given by eq 6 with $k_{fr} \gg k_2$. Actually, since

$$\eta_o = n\{k_2/(k_{fr} + k_2)\} \approx n(k_2/k_{fr}) \quad (6)$$

dioxanes 2b-1 are produced with efficiencies η_o between about 1 and 10, the energy-wasting process of fragmentation (k_{fr}) of biradical [•]1-1-O₂[•] should be several orders of magnitude more effective than the dioxane-forming cyclization (k_2).²⁵

Finally, the formation of 1,2-dioxane 2a from the strongly electron-donor substituted 1,1-diarylethylene 1a deserves some consideration.

(25) In order to check the feasibility of a 1,6-biradical (or 1,6-zwitterion) fragmentation into two olefinic molecules and molecular oxygen, the enthalpy change ΔH_f^\ddagger was estimated for CH₂CH₂CH₂CH₂OO as a model by performing a PM3 calculation²⁶ using the program package MOPAC.²⁷ The neutral molecule of lowest energy turned out to be a 1,6-biradical having almost the same electron densities at C-1 and the terminal oxygen atom. Furthermore, the conformation of lowest energy of the model 1,6-biradical is that shown for [•]1-1-O₂[•] in Scheme IV (with Ar₁ = Ar₂ = H). Fragmentation of this biradical into two molecules of ethylene and ³O₂ is slightly endothermic ($\Delta H_f^\ddagger = 4.66$ kcal mol⁻¹) but should occur with a positive entropy change ΔS_f^\ddagger large enough to yield an appreciably exergonic process ($\Delta G_f^\ddagger < 0$) at room temperature. Fragmentation may thus be associated with only a small or even negligible energy barrier ($\Delta G_f^\ddagger \approx 0$). Cyclization of the 1,6-biradical leading to a 1,2-dioxane should be associated with almost no activation enthalpy ($\Delta H_c^\ddagger \approx 0$) but with a relatively large negative activation entropy ΔS_c^\ddagger , thus yielding an appreciable energy barrier ΔG_c^\ddagger . With $\Delta G_f^\ddagger = 0$ and $\Delta G_c^\ddagger = -T\Delta S_c^\ddagger$, the ratio of rates of dioxane formation over fragmentation is given by $k_2/k_{fr} = \exp(\Delta S_c^\ddagger/R)$. For cyclization of neutral species, activation entropies of about -15 to -18 cal mol⁻¹ K⁻¹ appear to be reasonable values²⁸ which thus afford k_2/k_{fr} ratios of about 10⁻³-10⁻⁴. With these values for k_2/k_{fr} and $\eta_o = 1-10$ and [1] $\leq 2.5 \times 10^{-2}$ M, steady-state concentrations of O₂^{•-} ranging from about 10⁻⁵ to 10⁻⁷ M are calculated. This range of concentrations seems to be reasonable for O₂^{•-} under the reaction conditions used.

(26) (a) Stewart, J. J. P. *J. Comput. Chem.* 1989, 10, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* 1989, 10, 221.

(27) Stewart, J. J. P.; Seiler, F. S. *MOPAC*, Research Laboratory, US Air Force Academy, Colorado Springs, CO. QCPE Program No. 455, adapted to the PC by Serena Software, Bloomington, IN.

(28) Hoffmann, R. W. *Aufklärung von Reaktionsmechanismen*; Thieme: Stuttgart, 1976.

As is shown in Scheme III, interaction of ¹DCA* with ³O₂ gives rise to singlet oxygen, and since ³DCA* also transfers its energy to ³O₂ to give another singlet oxygen molecule, the limiting quantum yield of O₂(¹Δ_g) equals 2.^{18,29} In contrast to all the other 1,1-diarylethylenes studied here, 1a can transfer an electron to singlet oxygen in MeCN solution generating 1a^{•+} which reacts further in a chain reaction involving ³O₂ to afford dioxane 2a.^{12,30} Undoubtedly, 1a^{•+} is also formed by interaction of 1a with ¹DCA* but presumably with a rather small efficiency α_o because, due to the relatively low energy content of (1a^{•+}/DCA⁻)_{SSIP} ($\Delta G_{back} = -1.55$ eV), back-electron transfer should prevail over separation into SFRI. Since the contributions of the two pathways to the generation of 1a^{•+} have not been determined, values of v_L/v_o and $\alpha_o\eta_o$ for diarylethylene 1a are not shown in Table II.

Ketone Formation. 4,4'-Dimethoxybenzophenone (3b) is mainly, if not exclusively, formed by addition of singlet oxygen to 1b to give an unstable 1,2-dioxetane that cleaves into 3b + formaldehyde.^{12,13} In accord with this assertion, 3b formation is not observed when the photooxygenation of 1b is carried out in the presence of LP.

For the generation of benzophenones 3n-r, however, other pathways must be considered because 1,1-diphenylethylene 1n is inert toward O₂(¹Δ_g).⁶ Pathways which proceed via an intermediate 1,2-dioxetane, generated by interactions of 1n^{•+} with O₂^{•-} or ³O₂, are excluded because (1) tetracyanoanthracene (TCA) sensitizes the formation of 3n although the radical anion TCA⁻ cannot transfer its extra electron to ³O₂ and (2) addition of 1^{•+} to ³O₂ should be too slow to compete with the addition of 1n^{•+} to 1n yielding (1n-1n)^{•+}.⁹

Quite likely, benzophenones 3n-p (and perhaps also 3q and 3r) are formed from the 1,6-biradical [•]1-1-O₂[•] (Scheme IV) with a rate constant k_3 , in competition with 1,2-dioxane formation (k_2) and fragmentation into educts 1 and O₂(k_{fr}).

With this assumption, the efficiency $\eta_{(3)}$ of ketone formation is given by eq 7 with $k_{fr} \gg (k_2 + k_3)$.

$$\eta_{(3)} = n[k_3/(k_{fr} + k_2 + k_3)] \approx n(k_3/k_{fr}) \quad (7)$$

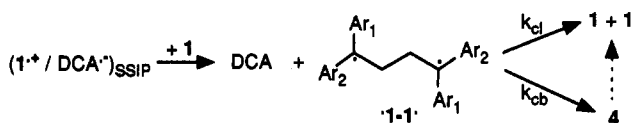
Since rose bengal photosensitized oxygenation of 1i in MeCN yields benzophenone 3i (but not dioxane 2i) in a very slow reaction, O₂(¹Δ_g) is likely to contribute to the benzophenone 3 formation from all the electron-donor substituted diarylethylenes 1c-1. However, the extent to which the O₂(¹Δ_g) pathway competes with that discussed for the 3n formation will vary with the number, nature, and position of the substituents. Apparently, the singlet oxygen pathway is favored by substituents of enhanced electron-donating properties. In spite of this, ketone formation decreases with increasing electron-donating properties of the aryl groups, indicating that these substituents favor 1,6-cyclization of [•]1-1-O₂[•] to dioxane 2 over ketone 3 formation (via 1,4-cyclization to an unstable 1,2-dioxetane and concomitant elimination of diarylethylene 1?) from this biradical.

Cyclobutane Formation. Cyclobutanes are observed in yields of about 10% from 1,1-diarylethylenes 1n-p. Mattes and Farid⁹ have shown that 4n is formed mainly by interaction of 1n with (1n^{•+}/DCA⁻)_{SSIP} and to a much lesser extent by electron transfer from 1n to cyclobutane

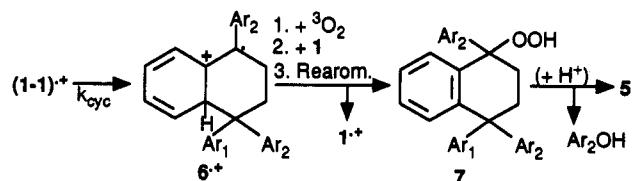
(29) Foote, C. S. *Tetrahedron* 1985, 41, 2221.

(30) Concomitantly with 1a^{•+}, superoxide O₂^{•-} is formed. It is interesting to note that the radical ions do not react with each other to give a 1,2-dioxetane that cleaves into ketone 3a and formaldehyde.¹²

Scheme V. Main Path of Cyclobutane (4) Formation⁹



Scheme VI. Proposed Mechanism of α -Tetralone (5) Formation



radical cation $4n^{•+}$, since its precursor $(1n-1n)^{•+}$ undergoes preferably a 1,6-cyclization to $6n^{•+}$ rather than a 1,4-cyclization to $4n^{•+}$. We assume that cyclobutanes **4o** and **4p** are formed correspondingly.

Cyclobutanes **4a–m** are not observed, indicating that the corresponding 1,4-biradicals $1-1^{\bullet}$, if formed at all, cleave immediately to two molecules of **1** either directly (k_{cl}) or via an unstable cyclobutane **4** (k_{cb}) (Scheme V).

α -Tetralone Formation. Whereas 1,4-cyclization of $(1-1)^{•+}$ to cyclobutane radical cation $4^{•+}$ may be negligible, 1,6-cyclization (k_{cyc}) to radical cation $6^{•+}$ is obviously prerequisite for the formation of α -tetralones **5m**, **5n**, and the isomeric mixture of **5o/5o'**. A conceivable path to **5** involves addition of 3O_2 to $6^{•+}$ followed by electron transfer from **1** and rearomatization to give the α -hydroperoxide **7** (and $1^{•+}$ that maintains the chain reaction). Subsequent (proton-catalyzed) rearrangement of **7** should lead to α -tetralone **5** (+ a phenol) as shown in Scheme VI.

Apparently, addition of 3O_2 to $(1-1)^{•+}$ (k_{ox}) is favored over 1,6-cyclization (k_{cyc}) when the positive charge of radical cation $(1-1)^{•+}$ can be delocalized efficiently by one of the aryl groups (*cf.* results obtained from diarylethylenes **1d**, **1e**, and **1g** with those from **1n**, **1o**, and **1q**, respectively).

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 acetonitrile; MeCN was therefore distilled over P_2O_5 and K_2CO_3 in sequence. 9,10-Dicyanoanthracene, mp 346–347 °C, was prepared from Bayer and Fritsch.³¹ Melting points are uncorrected.

¹H NMR spectra were recorded with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. IR spectra of solids were taken in KBr, those of fluids as films. Mass spectra were taken at various eV. UV spectra were recorded with $CHCl_3$ or CH_2Cl_2 as solvents.

Fluorescence quenching of deoxygenated MeCN solutions of DCA (1×10^{-5} M) by 1,1-diarylethylenes **1** was carried out at at least six different concentrations of these ethylenes between 0.001 and 0.03 M; excitation of DCA at 361 nm, determination of fluorescence intensities at 434 nm.

Oxidation 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 speeds at 100, 200, 300, and 400 mV/s. 1,1-Diarylethylenes **1** as well as their oxygenation products, 1,2-dioxanes **2**, showed irreversible oxidation potentials, E_{ox} , determined from the minima of the voltammograms by extrapolating to a scan speed at 0 mV/s. The

Table III. 1,1-Diarylethylenes (1): Procedures of Preparation, Melting Points, Boiling Points, and Literature Data

l	procedure	yield (%)	mp (°C)/ bp (°C/Torr)	lit. mp (°C)/ bp (°C/Torr)	ref
a	A	47	119–120	120–121	37
b	B	44	142–143	143–144	37
c	C	33	73–74	74	38
d	C	69	74–75	75	39
e	C	46	75–76	77	40
f	B	37	88–90	90	40
g	D	19	85–86	85.5	41
h	B	54	103–104	103–105	42
i	B	37	60–61	61	43
j	B	35	60–61		
k	C	62	96–97/0.5	160–161/11	44
l	A	83	103–105/12	136/5	45
m	B	33	130–132/0.5	190/10	46
n	A	63	133–134/12	135–136/13	47
o	A	66	159–160/12	164/16	40
p	A	75	89–90	91	40
q	D	41	64–65	66–66.5	48
r		32	175–176	175–176.5	36

instrument was calibrated by using 1,3,5-trimethoxybenzene ($E_{ox} = 1.49$ V)³² and tetrathiafulvalene ($E_{ox}^{1/2} = 0.33$ V, $E_{ox(2)}^{1/2} = 0.70$ V)³³ as standards for an irreversible and a reversible oxidation potential, respectively.

1,1-Diarylethylenes (1a–r). Symmetrically substituted 1,1-diarylethylenes were prepared either by reaction of diaryl ketone with CH_3MgI (1:1) (procedure A) or by reaction of $ArMgBr$ with ethyl acetate (2:1) (procedure B) in dry ether followed by water elimination in acetic acid (+ H_2SO_4) at 70–80 °C. Unsymmetrically substituted 1,1-diarylethylenes were prepared either by reaction of Ar_1MgBr with Ar_2COCH_3 (1:1) followed by water elimination (procedure C) or by a Wittig reaction of Ar_1COAr_2 with $(C_6H_5)_3P=CH_2$ (procedure D). The ketones and aryl bromides were purchased except 4-methoxyphenyl 4-nitrophenyl ketone, which was prepared after ref 34 (mp 121 °C), and *p*- $CD_3-C_6H_4Br$, which was prepared after ref 35 (bp 68–69 °C/12 Torr (lit.³⁵ bp 110 °C/83 Torr)). 1,1-Bis(4-nitrophenyl)ethylene (**1r**) was prepared by catalytic (Pd/C) hydrogenation of **1n** to the corresponding ethane that was subsequently transformed into **1r** after ref 36 by nitration with HNO_3 at –15 °C, reaction with *N*-bromosuccinimide/dibenzoyl peroxide in CCl_4 , and elimination of *HBr* with pyridine.

Photooxygenations of 1,1-Diarylethylenes. General Procedure for Analytical and Kinetic Runs. A 25-mL irradiation unit with automatic O_2 -consumption recording system⁴⁰ was used for oxygen-uptake studies. To obtain oxygen-saturated solutions, oxygen was bubbled through the solutions for 15 min before the irradiation cell was connected with the O_2 -containing burette. A mercury high-pressure lamp HP 125 W (Philips) was used as a light source. The reactions were run in the presence of DCA (2×10^{-4} M) and ethylenes **1** (initial concentrations: 0.025 M) (a) in the absence and (b) in the presence of 0.025 M $LiClO_4$. To

(32) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* 1964, 86, 4124.

(33) Coffen, D. L.; Chambers, J. Q.; Williams, D. R.; Garrett, P. E.; Canfield, N. D. *J. Am. Chem. Soc.* 1971, 93, 2258.

(34) Auwers, K. *Ber. Dtsch. Chem. Ges.* 1903, 36, 3890.

(35) Pollack, S. K.; Raine, B. C.; Hehre, W. J. *J. Am. Chem. Soc.* 1981, 103, 6308.

(36) Szmant, H. H.; Deffner, J. F. *J. Am. Chem. Soc.* 1959, 81, 958.

(37) Pfeiffer, P.; Wizinger, A. *Liebigs Ann. Chem.* 1928, 461, 132.

(38) McEwen, W. E.; Gilliland, M.; Sparr, B. J. *J. Am. Chem. Soc.* 1950, 72, 3212.

(39) Hurd, C. D.; Webb, C. N. *J. Am. Chem. Soc.* 1927, 49, 546.

(40) Bergmann, E.; Bondi, A. *Ber. Dtsch. Chem. Ges.* 1931, 64, 1455.

(41) Hegarty, A. F.; Lomas, J. S.; Wright, W. V.; Bergmann, E. D.; Dubois, J. E. *J. Org. Chem.* 1972, 37, 2222.

(42) Tarbell, D. S.; Lindstrom, E. G. *J. Am. Chem. Soc.* 1946, 68, 1930.

(43) Anschütz, R.; Hilbert, A. *Ber. Dtsch. Chem. Ges.* 1924, 57, 1697.

(44) Tiffeneau, M. *Ann. Chim. Phys.* 1907, 10, 360.

(45) Pines, H.; Arrigo, J. T. *J. Am. Chem. Soc.* 1958, 80, 4369.

(46) Wittig, G.; Gauss, W. *Chem. Ber.* 1947, 80, 363.

(47) Schlenk, W.; Bergmann, E. *Liebigs Ann. Chem.* 1928, 463, 1.

(48) Wittig, G.; Schöllkopf, U. *Chem. Ber.* 1954, 87, 1318.

(49) Gollnick, K.; Franken, T.; Fouda, M. F. R.; Paur, H. R.; Held, S. *J. Photochem. Photobiol., B: Biol.* 1992, 12, 57.

(31) Bayer, H.; Fritsch, H. *Ber. Dtsch. Chem. Ges.* 1941, 74, 494.

Table IV. 3,3,6,6-Tetraaryl-1,2-dioxanes (2): Initial Amounts of 1,1-Diarylethylenes 1, Yields, Melting Points, Molecular Weights, and Elemental Analyses of 2

1	1 g (mmol)	yield (2) g (%)	mp ^{a,b} (°C)	solva	mol. form. of 2	MW ^c calcd; found	C calcd; found	H calcd; found
a	2.67 (10)	2.48 (88)	181–182	T	C ₃₆ H ₄₄ N ₄ O ₂	564.76	76.56; 76.29	7.85; 7.75
b	1.20 (5)	1.15 (90)	211–212	EA	C ₃₂ H ₃₂ O ₆	512.58; 512, 517 ^d	74.98; 75.14	6.29; 6.32
c	1.12 (5)	0.94 (78)	188–192 ^e	EA/E	C ₃₂ H ₃₂ O ₄	480.58; 480	79.97; 80.20	6.71; 6.60
d	2.12 (10)	2.13 (94) ^f	156–161 ^g	EA/E	C ₃₀ H ₂₈ O ₄	452.52; 452, 458 ^d	79.62; 79.42	6.24; 6.38
e	2.48 (10)	2.01 (77) ^h	193–196 ⁱ	EA/E	C ₃₀ H ₂₆ Cl ₂ O ₄	521.41; 521, 510 ^d	69.10; 69.21	5.03; 4.96
f	1.20 (5)	1.01 (79)	216–217	T/E	C ₃₂ H ₃₂ O ₆	512.58; 512	74.98; 75.02	6.29; 6.21
g	1.27 (5)	1.03 (76) ^j	189–191	EA/E	C ₃₀ H ₂₆ N ₂ O ₈	542.53; 542	66.41; 66.42	4.83; 4.84
h	1.82 (5)	1.64 (86)	168–170	T/E	C ₃₂ H ₄₀ O ₆	760.84; 760	82.08; 81.97	5.30; 5.47
i	1.04 (5)	0.88 (78)	212–213	EA/E	C ₃₂ H ₃₂ O ₂	448.58; 448	85.68; 85.44	7.19; 6.98
j	0.214 (10) ^k	0.17 (74)	212–213	EA/E	C ₃₂ H ₂₀ D ₁₂ O ₂	460.68; 460	83.42; 83.67	4.58; 4.58 D = 5.24; 4.94 6.71; 6.52
k	0.97 (5)	0.79 (75) ^l	188–190 ^m 171–172 ^m	EA/E EA/E	C ₃₀ H ₂₈ O ₂ ^l	420.52; 420	85.68; 85.60	6.71; 6.52
l	1.04 (5)	0.76 (68) ⁿ	213–214 ^o 128–130 ^p	EA/E M	C ₃₂ H ₃₂ O ₂	448.58; 448	85.68; 85.77	7.19; 7.09
m	3.60 (15)	<0.2 (<5) ^q	213–215	EA/E	C ₃₂ H ₃₂ O ₆	512.61; 512	74.98; nd	6.29; nd
n	3.60 (20)	0.67 (17)	247–248	T	C ₂₈ H ₂₄ O ₂	392.47; 392	85.68; 85.83	6.16; 6.24
o	1.07 (5)	0.13 (11)	191–194	EA/E	C ₂₈ H ₂₂ Cl ₂ O ₂	461.36; 461	72.89; 73.00	4.81; 4.79
p	1.25 (5)	0.13 (10)	248–250	T/E	C ₂₈ H ₂₀ Cl ₄ O ₂	530.24; 530	63.42; 63.28	3.80; 3.90
q	0.11 (0.5) ^r							
r	0.68 (0.25) ^s							

^a Melting points after recrystallization from solvents: T = tetrahydrofuran; EA = ethyl acetate; E = ethanol; M = methanol. ^b Lit. mp's: 2a, 189–191 °C;⁸ 2b, 217–220 °C;⁷ 206.5–209 °C;⁸ 2i, 222–223.5 °C;⁷ 2n, 256–257 °C;⁷ 242–244 °C.⁸ ^c Molecular weight, generally determined by MS (20 eV). ^d Osmometrically in benzene. ^e *Cis/trans* mixture. ^f Residue, after rinsing with methanol: mixture of *cis* and *trans* isomers (≈1:1) (¹H NMR), mp 133–147 °C. ^g Mixture of *cis* and *trans* isomers ≈ 1:2 (¹H NMR). ^h Residue, after rinsing with methanol: mixture of *cis* and *trans* isomers (≈1:1) (¹H NMR), mp 175–187 °C. ⁱ Mixture of *cis* and *trans* isomers ≈ 4:3 (¹H NMR). ^j Residue, after heating in CH₂Cl₂/methanol (1:5) and removal of solvent mixture: *cis* and *trans* isomer mixture (1:1) (¹H NMR). ^k In 20 mL. ^l Residue, after heating in CH₂Cl₂/methanol (1:5) and removal of solvent mixture: *cis* and *trans* isomer mixture (1:1) (¹H NMR), mp 165–177 °C; elemental analysis performed with this mixture. ^m By slow cooling, two differently crystallized dioxanes were obtained, the one with the higher mp precipitating first. ⁿ Total yield. ^o Obtained from precipitate during the irradiation. ^p Obtained after isomer of higher mp was completely removed. ^q After column chromatography on silica gel, elution with toluene/CHCl₃ (9:1, v/v). ^r Addition of 41 mg (0.5 mmol) of biphenyl was necessary to achieve a slow O₂-consumption; only ketone 3p could be isolated. ^s Addition of 20 mg (0.25 mmol) of biphenyl yielded some ketone 3r in a very slow reaction.

cut off wavelengths shorter than 405 nm, a filter solution was placed between the lamp and the cell. The filter solution was prepared from 2.3 g of CuSO₄·5H₂O, 3.0 g of NaNO₂, and 5 mL of concd ammonia diluted with distilled water to 100 mL.

The products and product distributions were determined by ¹H NMR spectral analysis of the residues in CDCl₃, CCl₄, and benzene-*d*₆. The residues were obtained from irradiated solutions by removing MeCN at a rotatory evaporator, dissolving the residue, which still contains some MeCN, in 2 mL of CCl₄, and removing finally CCl₄ and the rest of MeCN on a rotatory evaporator.

Photooxygenation of 1,1-Diarylethylenes. 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-diarylethylenes 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 (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. To cut off wavelengths shorter than 405 nm, a filter solution was applied which was prepared as described above. 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.

Isolation and Characterization of 3,3,6,6-Tetraaryl-1,2-dioxanes 2a–p. Caution! All preparations, reactions, and workup procedures of peroxidic materials should ALWAYS be carried out behind safety shields since unexpected hazardous compounds may have been formed along with the desired compounds. Whereas dioxane 2a began to precipitate soon after the irradiation was started, the dioxanes from the other 1,1-diarylethylenes generally started to precipitate at the end of the irradiation period. After ~90% of the MeCN was removed at a rotary evaporator at room temperature, up to ~90% of the dioxanes precipitated and were filtered off. Removal of MeCN was completed, and the residues were recrystallized from the same solvents that were found to be appropriate for recrystal-

lization of the precipitates. When ketones (and other products) were formed along with the dioxanes, the corresponding ketones 3 (and products 4 and 5) were isolated from the filtrates obtained after recrystallization of the dioxanes.

Initial amounts of 1, yields, melting points, and elemental analyses (C and H only) of 2 are shown in Table IV. ¹H NMR, IR and UV data of 2 are as follows:

3,3,6,6-Tetrakis[4-(*N*-dimethylamino)phenyl]-1,2-dioxane (2a): ¹H NMR δ 2.48 (s, br, 4 H), 2.91 (s, 24 H), 6.83 (m, 8 Ar H), 7.14 (m, 8 Ar H); IR 2875, 2790, 1614, 1591, 1351, 1198, 943, 812 cm⁻¹; UV (CH₂Cl₂) λ_{max} = 272 nm (log ε = 4.66).

3,3,6,6-Tetrakis(4-methoxyphenyl)-1,2-dioxane (2b): ¹H NMR δ 2.48 (2, br, 4 H), 3.74 (s, 12 H), 6.84 (m, 8 Ar H), 7.22 (m, 8 Ar H); IR 2955, 2935, 2836, 1610, 1512, 1252, 1179, 1035, 828 cm⁻¹; UV (CH₂Cl₂) λ_{max} = 233 (log ε = 4.58), 273 nm (log ε = 3.88).

3,6-Bis(4-methoxyphenyl)-3,6-bis(4-methylphenyl)-1,2-dioxane (2c): ¹H NMR δ 2.28 (s, br, 6 H), 2.48 (s, br, 4 H), 3.71 (s, br, 6 H), 6.66–7.18 (m, 16 Ar H); IR 2955, 1610, 1512, 1510, 1253, 1180, 1036, 829, 812 cm⁻¹; UV (CHCl₃) λ_{max} = 268 (log ε = 3.60), 274 nm (log ε = 3.61).

3,6-Bis(4-methoxyphenyl)-3,6-diphenyl-1,2-dioxane (2d): ¹H NMR δ 2.51 (s, br, 4 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 6.59–7.58 (m, 18 Ar H); IR 1610, 1512, 1253, 1178, 1035, 830, 757, 700 cm⁻¹.

3,6-Bis(4-methoxyphenyl)-3,6-bis(4-chlorophenyl)-1,2-dioxane (2e): ¹H NMR δ 2.51 (s, br, 4 H), 3.74 (s, 3 H), 3.76 (s, 3 H), 6.64–7.56 (m, 16 Ar H); IR 2958, 2840, 1611, 1515, 1493, 1253, 1179, 1094, 1033, 1017, 998, 823 cm⁻¹.

3,3,6,6-Tetrakis(2-methoxyphenyl)-1,2-dioxane (2f): ¹H NMR δ 2.78 (s, br, 4 H), 3.40 (s, 12 H), 6.69–7.71 (m, 16 Ar H); IR 2935, 2833, 1598, 1583, 1492, 1490, 1435, 1291, 1253, 1028, 752 cm⁻¹; UV (CHCl₃) λ_{max} = 274 nm (log ε = 3.94).

3,6-Bis(4-methoxyphenyl)-3,6-bis(4-nitrophenyl)-1,2-dioxane (2g): ¹H NMR δ 2.59 (s, br, 4 H), 3.71 (s, 3 H), 3.76 (s, 3 H), 6.68–8.26 (m, 16 Ar H); IR 1608, 1514, 1348, 1255, 1181, 1034, 999, 853, 828 cm⁻¹; UV (CHCl₃) λ_{max} = 271 nm (log ε = 4.36).

3,3,6,6-Tetrakis(4-phenoxyphenyl)-1,2-dioxane (2h): ¹H NMR δ 2.52 (s, br, 4 H), 6.83–7.34 (m, 36 Ar H); IR 1588, 1507,

1505, 1490, 1241, 1170, 871, 754, 693 cm^{-1} ; UV (CH_2Cl_2) $\lambda_{\text{max}} = 238 \text{ nm}$ ($\log \epsilon = 3.70$).

3,3,6,6-Tetrakis(4-methylphenyl)-1,2-dioxane (2i): $^1\text{H NMR}$ δ 2.25 (s, 12 H), 2.49 (s, br, 4 H), 6.95–7.20 (m, 16 Ar, H); IR 3026, 2964, 2940, 2920, 1511, 1448, 1188, 1074, 1000, 814, 789, 555 cm^{-1} ; UV (CHCl_3) $\lambda_{\text{max}} = 264$ ($\log \epsilon = 3.34$), 273 nm ($\log \epsilon = 3.74$).

3,3,6,6-Tetrakis(4-methyl-*d*₅-phenyl)-1,2-dioxane (2j): $^1\text{H NMR}$ δ 2.50 (s, br, 4 H), 7.08 (s, br, 16 Ar H); IR 3027, 2965, 2129, 1700, 1512, 1409, 1188, 1070, 1000, 887, 793, 781, 698; UV (CHCl_3) $\lambda_{\text{max}} = 264$ ($\log \epsilon = 3.27$), 273 nm ($\log \epsilon = 3.12$).

3,6-Bis(4-methylphenyl)-3,6-diphenyl-1,2-dioxane (2k): $^1\text{H NMR}$ δ 2.25 (s, br, 6 H), 2.51 (s, br, 4 H), 7.06–7.21 (m, 18 Ar H); IR 2965, 1700, 1492, 1446, 1003, 945, 815, 754, 697 cm^{-1} ; UV (CHCl_3) $\lambda_{\text{max}} = 258$ ($\log \epsilon = 3.53$), 264 nm ($\log \epsilon = 3.50$).

3,6-Bis(2,4-dimethylphenyl)-3,6-diphenyl-1,2-dioxane (2l): first compound, mp 213–214 °C; $^1\text{H NMR}$ δ 2.01 (s, 6 H), 2.33 (s, 6 H), 2.60 (s, br, 4 H), 6.84–7.48 (m, 16 Ar H); second compound, mp 128–130 °C; $^1\text{H NMR}$ δ 2.01 (s, 6 H), 2.23 (s, 6 H), 2.56 (s, br, 4 H), 6.77–7.25 (m, 16 Ar H); mixture IR 2966, 1447, 956, 814, 755, 699 cm^{-1} ; UV (CHCl_3) $\lambda_{\text{max}} = 253$ ($\log \epsilon = 3.06$), 260 nm ($\log \epsilon = 3.11$).

3,3,6,6-Tetrakis(3-methoxyphenyl)-1,2-dioxane (2m): $^1\text{H NMR}$ δ 2.51 (s, br, 4 H) 3.69 (s, 12 H), 6.62–7.25 (m, 16 Ar H).

3,3,6,6-Tetraphenyl-1,2-dioxane (2n): $^1\text{H NMR}$ δ 2.57 (s, br, 4 H), 7.25 (m, 20 Ar H); IR 3085, 3058, 1495, 1449, 1215, 1064, 1008, 954, 915, 769, 751, 696, 582 cm^{-1} ; UV (CHCl_3) $\lambda_{\text{max}} = 258$ nm ($\log \epsilon = 3.61$).

3,6-Bis(4-chlorophenyl)-3,6-diphenyl-1,2-dioxane (2o): $^1\text{H NMR}$ δ 2.50 (s, br, 4 H), 7.19 (s, br, 18 Ar H).

3,3,6,6-Tetrakis(4-chlorophenyl)-1,2-dioxane (2p): $^1\text{H NMR}$ δ 2.46 (s, br, 4 H), 7.19 (m, 16 Ar H); IR 1594, 1492, 1095, 1070, 1014, 1000, 939, 819, 541, 517, 500 cm^{-1} ; UV (CHCl_3) $\lambda_{\text{max}} = 266$ ($\log \epsilon = 3.24$), 276 nm ($\log \epsilon = 3.04$).

4,4'-Dimethoxybenzophenone (3b): colorless crystals; mp 141–142 °C (lit.⁵⁰ mp 144 °C).

4-Methoxy-4'-methylbenzophenone (3c): mp 90 °C (lit.⁵¹ mp 90–91 °C).

4-Chloro-4'-methoxybenzophenone (3e): mp 126–127 °C (lit.⁴⁰ mp 127 °C).

2,2'-Dimethoxybenzophenone (3f): mp 103–104 °C (lit.⁵² mp 104 °C).

4-Methoxy-4'-nitrobenzophenone (3g): Prepared after the method of Auwers⁵⁴ described above. Mp 121 °C.

4,4'-Diphenoxybenzophenone (3h): mp 147 °C (lit.⁵³ mp 147 °C).

4,4'-Dimethylbenzophenone (3i): mp 94–95 °C (lit.⁵⁴ mp 95 °C).

4-Methylbenzophenone (3k): mp 58–60 °C (lit.⁵⁵ mp 59–60 °C).

2,4-Dimethylbenzophenone (3l): liquid; identified by spectroscopic comparison with a purchased sample.

3,3'-Dimethoxybenzophenone (3m): bp 122–125 °C/0.5 Torr (lit.⁵⁶ bp 195–196 °C/11 Torr).

4,4-Bis(3-methoxyphenyl)-7-methoxy-1-tetralone (5m): After removal of MeCN from the irradiated solution of 1m, the oily residue was separated by column (60 cm) chromatography on silica gel, elution with toluene/ CHCl_3 (9:1, v/v). 5m (0.38 g, 13%): mp 109–110 °C (from methanol), along with 1 g (28%) of 3m and less than about 5% of 2m.

5m: $^1\text{H NMR}$ δ 2.48 and 2.86 (m, 4 H), 3.65 (s, 6 H), 3.80 (s, 3 H), 6.50–7.20 (m, 10 Ar H), 7.50 (d, 1 Ar H); IR 1681, 1606, 1582, 1487, 1424, 1318, 1247, 1235, 1045, 779, 703 cm^{-1} ; UV (CHCl_3) $\lambda_{\text{max}} = 255$ ($\log \epsilon = 4.01$), 281 ($\log \epsilon = 3.71$), 323 nm ($\log \epsilon = 3.60$); MS 388 (M^+).

Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{O}_4$ (388.44): C, 77.30; H, 6.23. Found: C, 77.15; H, 6.07.

Benzophenone (3n), 1,1,2,2-Tetraphenylcyclobutane (4n), and 4,4'-Diphenyl-1-tetralone (5n): After removal of (precipitated) 2n and MeCN, the oily residue was separated by column

chromatography on silica gel, elution with ether/petroleum ether (varying from 1:9 to 1:5, v/v). 4n (75 mg, 2%), mp 111–112 °C (from ethanol), and 5n (90 mg, 3%), mp 184–185 °C (from ethanol), were obtained along with 3n (1.4 g, 40%), mp 47 °C (identical with a purchased sample).

4n: $^1\text{H NMR}$ δ 3.17 (s, br, 4 H), 6.93 (m, 20 Ar H); IR 2982, 1599, 1494, 1442, 1036, 778, 766, 710, 610 cm^{-1} ; UV (CHCl_3) $\lambda_{\text{max}} = 266$ nm ($\log \epsilon = 3.22$); MS 360 (M^+).

Anal. Calcd for $\text{C}_{28}\text{H}_{24}$ (360.47): C, 93.29; H, 6.71. Found: C, 93.14; H, 6.62.

5n: $^1\text{H NMR}$ δ 2.49 (t, 2 H), 2.96 (t, 2 H), 6.64–6.75 (m, 1 Ar H), 6.91–7.39 (m, 12 Ar H), 8.02–8.14 (m, 1 Ar H); IR 3058, 1681, 1594, 1497, 1446, 1331, 1285, 1240, 1212, 766, 762, 702, 556 cm^{-1} ; MS 298 (M^+) (spectroscopic data: see ref 57).

Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{O}$ (298.36): C, 88.56; H, 6.08. Found: C, 88.53; H, 5.99.

4-Chlorobenzophenone (3o), 1,2-Bis(4-chlorophenyl)-1,2-diphenylcyclobutane (4o), and mixture of 4-(4-Chlorophenyl)-4-phenyl-1-tetralone (5o) and 6-Chloro-4-(4-chlorophenyl)-4-phenyl-1-tetralone (5o'). After removal of (precipitated) 2o and MeCN, the oily residue dissolved in 30 mL of methanol and kept at –10 °C for 2 days yielded 3o (0.4 g, 37%), mp 75–76 °C (lit.⁵⁸ mp 75–77 °C). In another experiment, the oily residue was separated by column chromatography on silica gel, elution with CHCl_3 /benzene (varying from 1:9 to 3:7, v/v). Along with 3o, cyclobutane 4o (attempted recrystallization from various solvents resulted only in dissociation into ethylene 1o; identification by MS and $^1\text{H NMR}$ by comparison with that of 4p) and a mixture of tetralones 5o and 5o', mp 144–148 °C (from methanol after 2 days at –10 °C) were obtained.

4o: $^1\text{H NMR}$ δ 3.08 (s, br, 4 H), 6.59–7.58 (m, 18 Ar H); $\text{C}_{22}\text{H}_{22}\text{Cl}_2$ (429.36), MS 430 ($\text{M}^+ + 1, 1$), 428 ($\text{M}^+ - 1, 2$).

5o,5o': $^1\text{H NMR}$ δ 2.48 (t, 2 H), 2.92 (t, 2 H), 6.68 (m, 1 Ar H), 6.85–7.40 (m, 11 Ar H), 8.06 (m, 1 Ar H); $\text{C}_{22}\text{H}_{17}\text{OCl}$ (332.81) (5o), MS 332 (M^+ , 100); $\text{C}_{22}\text{H}_{18}\text{OCl}_2$ (367.25) (5o'), MS 368 ($\text{M}^+ + 1, 5$).

4,4'-Dichlorobenzophenone (3p) and 1,1,2,2-Tetrakis(4-chlorophenyl)cyclobutane (4p): After removal of MeCN, the yellowish oily residue was dissolved in hot ethyl acetate/ethanol (1:5, v/v), from which after being cooled to room temperature 130 mg (10%) of dioxane 2p precipitated. The residue obtained after the solvent mixture was distilled off was dissolved in CH_2Cl_2 ; after addition of methanol, 4p precipitated, was filtered off, and was recrystallized from methanol: mp 79–80 °C. Ketone 3p was isolated from the CH_2Cl_2 /methanol filtrate and identified by comparison with a purchased authentic sample.

4p: $^1\text{H NMR}$ δ 3.08 (s, br, 4 H), 6.71 (d, 8 Ar H), 7.00 (d, 8 Ar H); IR 1610, 1492, 1488, 1394, 1092, 1015, 1012, 905, 900, 846, 835, 512 cm^{-1} ; UV (CHCl_3) $\lambda_{\text{max}} = 273$ ($\log \epsilon = 4.79$), 281 nm ($\log \epsilon = 4.67$); MS 498 (M^+).

Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{Cl}_4$ (498.24): C, 67.49; H, 4.05. Found: C, 67.57; H, 4.06.

4-Nitrobenzophenone (3q) and 4,4'-Dinitrobenzophenone (3r): Ketone 3q, mp 136–138 °C (identified by comparison with a purchased authentic sample). Ketone 3r: mp 188–189 °C (lit.⁵⁹ mp 189 °C).

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(50) Schnackenberg, H.; Scholl, R. *Ber. Dtsch. Chem. Ges.* 1903, 36, 654.

(51) Orékhoff, A.; Brouty, J. *Bull. Soc. Chim. Fr.* 1930, 47, 621.

(52) Graebe, C.; Feer, A. *Ber. Dtsch. Chem. Ges.* 1886, 19, 2610.

(53) Tadros, W.; Latif, A. *J. Chem. Soc. (London)* 1949, 3337.

(54) Weiler, J. *Ber. Dtsch. Chem. Ges.* 1874, 7, 1183.

(55) Zincke, T. *Liebigs Ann. Chem.* 1872, 161, 108.

(56) Ullmann, F.; Goldberg, I. *Ber. Dtsch. Chem. Ges.* 1902, 35, 2811.

(57) Repinskaya, I. B.; Abramov, A. D.; Kuklina, N. A.; Koptnyg, V. *A. J. Org. Chem. USSR* 1979, 15, 1973.

(58) Demuth, R.; Dittrich, M. *Ber. Dtsch. Chem. Ges.* 1890, 23, 3609.

(59) Staedel, W. *Ber. Dtsch. Chem. Ges.* 1894, 27, 2109.