Electron-Transfer Photosensitized Oxygenation of Stilbene and Naphthalene Derivatives in the Presence of Acetate Ion. Controlling the Reaction of the Cation Radicals by Weak-Nucleophilic Salts

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(Received September 14, 1992)

The 9,10-Dicyanoanthracene (DCA)- or 9-cyanoanthracene-sensitized photooxygenation of *trans*-stilbene derivatives gave benzaldehyde derivatives efficiently in the presence of weak-nucleophilic salts, such as Et₄NOAc and KOAc/18-crown-6 ether. The product distribution of this photooxygenation was apparently different from that of each photooxygenation in the presence of $Mg(ClO_4)_2$ and Et_4NBF_4 or in the absence of the salt. The DCA-sensitized photooxygenation of 2-methylnaphthalene gave phthalic acid and 4-methylphthalic acid in the presence of Et₄NOAc. These products were different from the products generated from each photooxygenation in the presence of Et_4NBF_4 and $KClO_4$ or in the absence of the salt. Also, such ring-oxygenation occurred in the DCA-sensitized photooxygenation of 2,3-dimethylnaphthalene and naphthalene in the presence of Et₄NOAc. These photooxygenations in the presence of Et₄NOAc proceeded by the addition of an acetate ion to the cation radical of the substrate generated by a photochemical electron transfer from the substrate to the sensitizer and the subsequent reaction with O_2 and the related oxygen species.

A large amount of interest in photochemical electron transfer reactions has been directed toward the controlling outcome of these processes.[1] The addition of salts is often effective to control photoreactions proceeding through exciplexs and ion radicals, since the charge separation and chemical reactivities of the ion radicals may be affected by interactions with salt ions as well as by a salt-induced increase in the solvent polarity.[2] Such salt effects can generally bring about remarkable changes in the reaction efficiencies, but usually produce no alteration of the reaction courses.[3,4] On the other hand, a nucleophile is well known to interact with cation radicals, resulting in the formation of a nucleophile-incorporated product in many cases. Therefore, nucleophiles have been used to trap cation species and for synthetic purposes. We expected that a weak-nucleophilic salt may change the reaction courses of the cation radicals without the formation of any nucleophile-incorporated products. In a preliminary report we reported that the addition of Et₄NOAc changed the reaction courses of the photooxygenation of naphthalene derivatives.[5] In order to elucidate the effect of weak-nucleophilic salts on the photooxygenation via electron transfer, we now report on the photooxygenation of stilbene and naphthalene derivatives in the presence of Et₄NOAc as well as other weak-nucleophilic salts.

Results

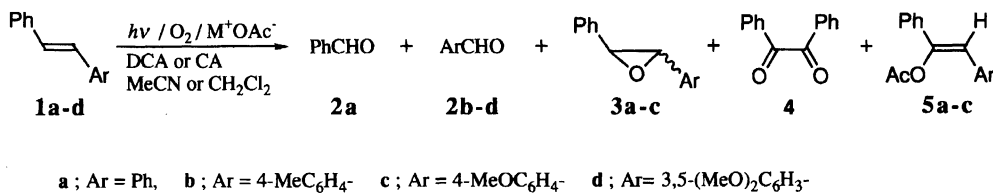### Photooxygenation of Stilbene Derivatives (1).

To find effective weak-nucleophilic salts regarding photosensitized oxygenation, we performed a 9,10-dicyanoanthracene (DCA)-sensitized photooxygenation of *trans*-stilbene (1a) in the presence of $Et_4N^+X^-$ (X= OAc and OTs) or a complex of potassium salts (K^+X^-, X=OAc, OCN, OCOCF₃, and SCN) with 18-crown-6 ether. The photooxygenation was carried out by ir-

radiating (>400 nm) an O_2-saturated acetonitrile solution (40 cm³) containing 1a (2 mmol), DCA (0.02 mmol), and the salt (4 mmol) by a high-pressure mercury lamp using an aqueous $CuSO_4/NH_3$ filter solution. The results are summarized in Table 1. The DCA-sensitized photooxygenation of 1a in the presence of Et₄NOAc gave benzaldehyde 2a (62%), *trans*-2,3-diphenyloxirane (3a, 7%), benzil (4, 1%), and 1-acethoxy-1,2-diphenylethene (5a, 9%) (Run 1), as shown in Scheme 1. Table 1 shows that the addition of Et₄NOAc or KOAc/18-crown-6 ether was effective for the formation of 2a, since the DCA-sensitized photooxygenation of 1a in the absence of the salt (Run 9) gave 2a, 3a, and 4 in 33, 15, and 4% yields, respectively, as has been reported by Foote et al.[6] Although the addition of Et₄NOTs or KOCN/18-crown-6 ether was moder-

Table 1. DCA-Sensitized Photooxygenation of *trans*-Stilbene (1a) in the Presence of the Weak- or the Non- Nucleophilic Salts in MeCN[a]

Run No.	Salt[b]	Product yield/%[c]				Recovery of 1a/% (Z : E)[d]
		2a	3a	4	Others	
1	Et₄NOAc	62	7	1	5a 9	31 (7 : 3)
2	Et₄NOTs	53	8	5		0
3	KOAc/18-C-6	63	6	1	5a 9	11 (8 : 2)
4	KOCN/18-C-6	43	1	1		22 (1 : 9)
5	KOCOCF₃/18-C-6	38	17	6		1 (6 : 4)
6	KSCN/18-C-6	29	15	3		7 (4 : 6)
7	Ng(ClO₄)₂	34	18	0		0
8	Et₄NBF₄	34	11	1		0
9	None[e]	33	15	4		0

a) For an O_2-saturated acetonitrile (40 cm³) solution containing 1a (2 mmol), DCA (0.02 mmol) and the salt (4 mmol). b) 18-C-6; 18-crown-6 ether. c) GLC yields based on consumed 1a. d) Isomer ratio of *cis*- to *trans*-1a. e) In the absence of the salt.

Scheme 1.

Table 2. CA-Sensitized Photooxygenation of *trans*-Stilbene Derivatives (**1a—d**) in the Presence of Et_4NOAc[a]

Run No.	1	Solvent	Product (Yield/%)[b]				Recovery of 1/% $(Z : E)$[c]
10	**1a**	MeCN	**2a**(79)				20 (5 : 5)
11	**1a**[d]	MeCN	**2a**(37)		**3a**(13)	**4**(4)	29 (4 : 6)
12	**1b**	MeCN	**2a**(82)	**2b**(77)			0
13	**1b**[d]	MeCN	**2a**(28)	**2b**(24)	**3b**(24)		7 (7 : 3)
14	**1c**	MeCN	**2a**(93)	**2c**(66)			0
15	**1c**[d]	MeCN	**2a**(31)	**2c**(19)	**3c**(65)		38 (4 : 6)
16	**1d**	MeCN	—[e]				100 (6 : 4)
17[f]	**1d**	MeCN	**2a**(53)	**2d**(44)			61 (7 : 3)
18	**1b**	CH_2Cl_2	**2a**(32)	**2b**(23)		**5b**(44)	72 (3 : 7)
19	**1c**	CH_2Cl_2	**2a**(46)	**2c**(34)	**3c**(20)	**5c**(10)	5 (0 : 1)

a) For an O_2-saturated MeCN or CH_2Cl_2 (40 cm³) solution containing 1 (1 mmol), CA (0.02 mmol) and Et_4NOAc (4 mmol). b) GLC yields based on consumed 1. c) Isomer ratio of *cis*- to *trans*-1. d) In the absence of Et_4NOAc. e) No reaction. f) DCA-sensitized photooxygenation.

ately effective, the addition of $KOCOCF_3$/18-crown-6 ether or KSCN/18-crown-6 ether was not effective. It was confirmed that the effect of Et_4NOAc was different from the usual effects of nonnucleophilic salts, such as $Mg(ClO_4)_2$ and Et_4NBF_4, since DCA-sensitized photooxygenation in the presence of $Mg(ClO_4)_2$ or Et_4NBF_4 (Runs 7 and 8) gave a similar product distribution as that in the absence of the salt (Run 9). Therefore, Et_4NOAc was used as a weak-nucleophilic salt throughout the present investigation.

The photooxygenations of substituted *trans*-stilbenes (**1b—d**) in the presence of Et_4NOAc in MeCN were carried out by using 9-cyanoanthracene (CA) as a sensitizer (Table 2), since the yield of **2a** was improved in CA-photosensitization, i.e. the CA-sensitized photooxygenation of **1a** gave exclusively **2a** in 79% yield (Run 10). The CA-sensitized photooxygenation of *trans*-4-methylstilbene (**1b**) and *trans*-4-methoxystilbene (**1c**) in the presence of Et_4NOAc (Runs 12 and 14) gave 4-methylbenzaldehyde (**2b**) and 4-methoxybenzaldehyde (**2c**), respectively, as well as the formation of **2a**. The CA-sensitized photooxygenation of **1a**, **1b**, and **1c** in the absence of Et_4NOAc gave the corresponding benzaldehydes (**2**) in low yields, accompanying the formation of **3a**, a mixture of *cis*- and *trans*-2-phenyl-3-(4-methylphenyl)oxirane (**3b**), and a mixture of *cis*- and *trans*-2-phenyl-3-(4-methoxyphenyl)oxirane (**3c**), respectively (Runs 11, 13, and 15). Figure 1 shows the time-conversion curves for the CA-sensitized photooxygenation of

1b in the presence of Et_4NOAc. Although the formation of **2a** and **2b** increased with an increase in conversion, **3b** was not formed, even at low conversion. It was found that the addition of Et_4NOAc entirely suppressed the formation of **3b**.

The CA-sensitized photooxygenation of **1b** and **1c** in CH_2Cl_2 gave considerable amounts of acetoxyl group-incorporated compounds, a mixture of *cis*- and *trans*-1-acetoxy-2-(4-methylphenyl)-1-phenylethene (**5b**) and a
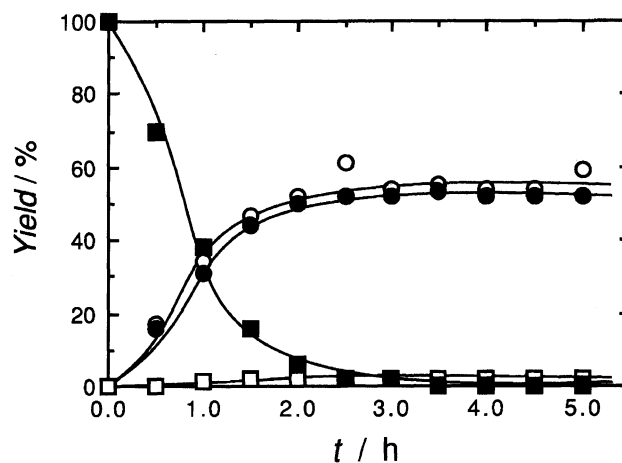

Fig. 1. Time-conversion curves for the disappearance of **1b** (-■-) and for the formation of **2a** (-○-), **2b** (-●-), and **3b** (-□-) for the CA-sensitized photooxygenation of **1b** in the presence of Et_4NOAc.

Table 3.   DCA-Sensitized Photooxygenation of Naphthalene Derivatives (6a—c) in the Presence of the Salts[a]

Run No.	6	Salt[b]	Irradn. time / h	Product (Yield/%)[c]		Conversion of 6/%
20	6a	Et$_4$NOAc	7	7a(21)	7c(14)	74
21	6a	Et$_4$NOAc	1	7a(10)	7c(7)	15
22	6a	KOAc/18-C-6	6	7a(27)	7c(17)	63
23	6a	KClO$_4$	0.5	8 (12)		11
24	6a	Et$_4$NBF$_4$	1	9 (37)		15
25	6a	None	0.3	8 (26)		7
26	6b	Et$_4$NOAc	9	7b(39)	7c(22)	94
27	6c	Et$_4$NOAc	7	7c(50)		67
28[d,e]	6a	Et$_4$NOAc	41	7a(17)	7c(12)	68
29[d,e]	6a	None	10	9 (24)		78
30[e]	6a	Et$_4$NOAc	22	7a(9)	7c(9)	81
31[e]	6a	None	50	9 (44)		78

a) For an O$_2$-saturated acetonitrile (40 cm^3) solution containing 6 (1 mmol), DCA (0.04 mmol) and the salt (4 mmol).   b) 18-C-6; 18-crown-6 ether, none; in the absence of the salt.   c) HPLC yields based on consumed 6.   d) Irradiation without using an aqueous CuSO$_4$-NH$_3$ filter.   e) For a dichloromethane solution.
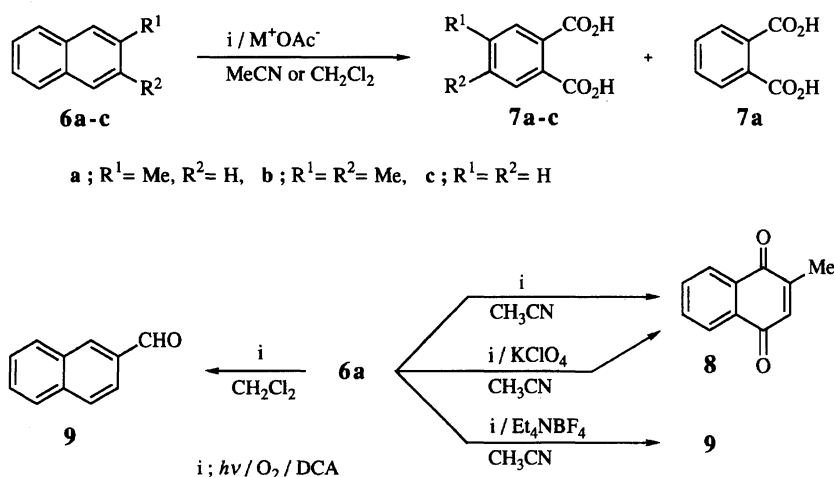
Scheme 2.

mixture of cis- and trans-1-acetoxy-2-(4-methoxyphenyl)-1-phenylethene (5c), as well as the formation 2 and 3, while 5b and 5c were not formed from the photooxygenation in MeCN. Moreover, although the CA-sensitized photooxygenation of trans-3,5-dimethoxystilbene (1d) did not proceed in MeCN and CH$_2$Cl$_2$ at all, the DCA-sensitized photooxygenation of 1d gave 2a and 2d.

Photooxygenation of Naphthalene Derivatives (6).   Also, the effect of Et$_4$NOAc was investigated concerning the DCA-sensitized photooxygenation of 6. The results are summarized in Table 3 and Scheme 2. The photooxygenation of 2-methylnaphthalene (6a) in the presence of Et$_4$NOAc or KOAc/18-crown-6 ether (Runs 20 and 22) gave 4-methylphthalic acid (7a) and phthalic acid (7c), whereas the photooxygenation in the absence of Et$_4$NOAc gave only 2-methyl-1,4-naphthoquinone (8) (Run 25). By contrast, Et$_4$NBF$_4$ and KClO$_4$ were not effective in the formation of 7 at all; the

photooxygenation of 6a gave 8 in the presence of KClO$_4$ (Run 23) and 2-naphthaldehyde (9) in the presence of Et$_4$NBF$_4$ (Run 24) at a low conversion of 6a (<15%), though further irradiation resulted in the consumption of 8 and 9 without the accumulation of any other definite products. Similarly, the photooxygenation of 2,3-dimethylnaphthalene (6b) and naphthalene (6c) in the presence of Et$_4$NOAc gave the corresponding phthalic acids (7) (Runs 26 and 27). Moreover, although the photooxygenation of 6a in CH$_2$Cl$_2$ gave again 7a and 7c in the presence of Et$_4$NOAc (Runs 28 and 30), it gave 9 in the absence of Et$_4$NOAc (Runs 29 and 31).[7]

Quenching Experiment.   Fluorescence quenching of DCA or CA by 1a—d in MeCN and CH$_2$Cl$_2$ gave the Stern–Volmer constants (K_{sv}) and the quenching rate constants (k_q) listed in Table 4. The fluorescence of DCA was efficiently quenched by Et$_4$NOAc, while the fluorescence of CA was inefficiently quenched by Et$_4$NOAc.

Table 4. Fluorescence Quenching of DCA and CA by
Stilbene Derivatives (1a—d) and Et$_4$NOAc

Sensitizer	Solvent	Quencher	K_{sv}[a] dm^3 mol^{-1}	$k_q \times 10^{10}$[b] dm^3 mol^{-1} s^{-1}
DCA	MeCN	1a	248	1.6
	MeCN	1d	300	2.0
	MeCN	Et$_4$NOAc	192	1.3
CA	MeCN	1a	—	0.36[c]
	MeCN	1b	153	0.75
	MeCN	1c	210	1.0
	MeCN	1d	90	0.44
	MeCN	Et$_4$NOAc	<13	<0.06
	CH$_2$Cl$_2$	1b	86	0.9
	CH$_2$Cl$_2$	1c	193	2.0
	CH$_2$Cl$_2$	Et$_4$NOAc	8	0.09

a) Stern–Volmer constants for the fluorescence quench-
ing. b) Rate constants for the fluorescence quenching;
τ_f=15.3 ns (DCA) in MeCN, τ_f=20.5 ns (CA) in MeCN,
and τ_f=9.4 ns (CA) in CH$_2$Cl$_2$. c) The value from
Ref. 6a.

Discussion

Mechanism. As has been reported for stilbene
by Foote et al.[6] and for naphthalene derivatives by
Santamaria,[8] an electron transfer from 1a or 6a—c
to the excited singlet state of DCA or CA is responsi-
ble for the initiation process of the photooxygenation in
the absence or presence of the salts. Also, the photo-
oxygenation of 1b and 1c is certainly initiated by a
photochemical electron transfer from 1b or 1c to CA,
since the florescence of CA were efficiently quenched by
1b and 1c.

In the absence of the salt or in the presence of the
nonnucleophilic salts, the resulting cation radicals of 1
react directly with O$_2^{-\cdot}$ generated by the reduction of
the anion radicals of CA or DCA to produce 2 and 3
(Scheme 3).[6] In the presence of M$^+$OAc$^-$(M=Et$_4$N
and K/18-crown-6 ether), it is proposed that OAc$^-$ re-
acts with 1$^{+\cdot}$ to give an adduct (10; ·1-OAc) in compe-
tition with O$_2^{-\cdot}$, as shown in Scheme 4. The adduct, 10,
readily undergoes a radical coupling reaction with O$_2^{-\cdot}$
to give an intermediate (11; $^-$OO-1-OAc). Elimination
of the acetoxyl group from 11 gives a dioxetane, since
an acetoxyl group is a good leaving group. The diox-
etane is well known to be a precursor for the formation
of 2.[9] Therefore, the formation of 11 is a key path-
way for the formation of 2 in the presence of M$^+$OAc$^-$.
Farid et al. have reported that both a nucleophile- and
oxygen-incorporated intermediate was formed as an in-
termediate for the photooxygenation of 1,1-dimethylin-
dene.[10] The formation of an adduct (·1-OAc) inhibits
any direct reaction of 1$^{+\cdot}$ with O$_2^{-\cdot}$, resulting in the
lack of 3. It has been confirmed that no formation of
2 occurred from the degradation of 3 by the reaction
with OAc$^-$ or O$_2$, since the DCA-sensitized photooxy-
genation of 3 in the presence of M$^+$OAc$^-$ did not give

2. Photooxygenation in the presence of the other weak
nucleophiles, such as Et$_4$NOTs and KOCN/18-crown-6
ether, proceeds, to some extent, in a similar way as in
the case of M$^+$OAc$^-$.

The formation of 10 was strongly supported by the
formation of the acetoxyl group-incorporated prod-
uct (5) during photooxygenation in the presence of
M$^+$OAc$^-$. The formation of 5 proceeds by the nucle-
ophilic addition of OAc$^-$ to 1$^{+\cdot}$, followed by the oxida-
tion with O$_2$ and subsequent deprotonation. Moreover,
the acetoxylation of 1c occurred selectively at the ben-
zylic position of the phenyl group. This result is in
accord with the selectivity of the photoamination of 1c
with ammonia, which proceeds by the nucleophilic ad-
dition of ammonia to the benzylic position of the phenyl
group of 1c$^{+\cdot}$.[11]

Moreover, the photooxygenation of naphthalene
derivatives (6) in the presence of M$^+$OAc$^-$ occurs
through a similar mechanism to the case of 1; the re-
action of the adduct radical (·6-OAc) with O$_2$ and/or
related oxygen species gave 7a—c as the final prod-
ucts, though mechanistic details for the follow-up proc-
esses are still unknown (Scheme 5).[5] The specific oxy-
genation of the aromatic rings can be explained by this
mechanism. Two kinds of phthalic acids were produced
by the addition of OAc$^-$ to both the substituted and
unsubstituted ring of 6a or 6b.[12] In accord with this
mechanism, a lack of the formation of 7 in the presence
of Et$_4$NBF$_4$ or KClO$_4$ can be easily explained in terms
of the negligible or very weak nucleophilicity of BF$_4^-$
and ClO$_4^-$. It is of synthetic significance to note that
the selective oxidative cleavage of the aromatic rings by
the DCA-sensitized photooxygenation of 6 in the pres-
ence of M$^+$OAc$^-$ is in sharp contrast to the usual photo-
oxygenations of alkylated arenes that generally result in
the oxidation of alkyl substituents.[13]

Conclusion

These mechanistic speculations have been born out
of our previous studies concerning the efficient addition
of such nucleophiles as CN$^-$,[14] BH$_4^-$,[15] and RNH$_2$[16]
to photogenerated cation radicals of aromatic hydro-
carbons and stilbenes. The effect of nonnucleophilic
salts, such as Mg(ClO$_4$)$_2$, on the photooxygenation via
electron transfer has been understood by the stabiliza-
tion of ion radicals by Coulombic interaction, resulting
in the suppression of a back electron transfer between
ion radicals.[3] The weak-nucleophilic salts bring about
the unusual effects that are caused by nucleophilic ad-
ditions to the cation radical, as well as complexation
with the ion radicals. Thus, the present investigation
reveals that the reaction courses of photooxygenation
via electron transfer can be controlled by the use of non
or weak-nucleophilic salts, as well as by the choice of
solvents.
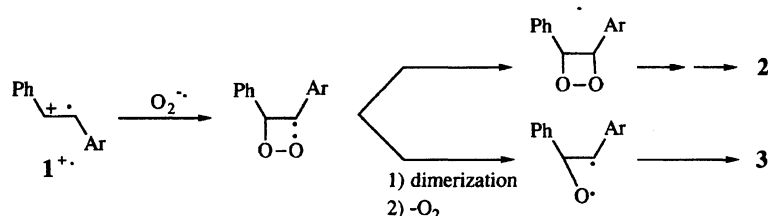
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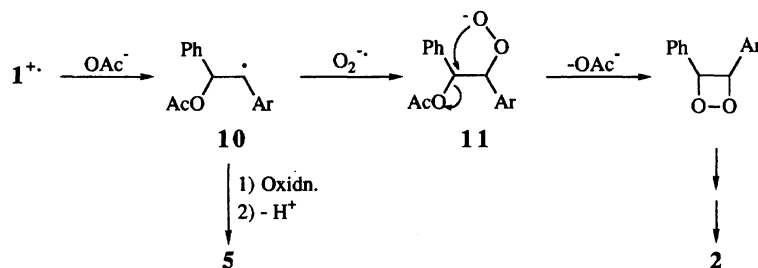
Scheme 4.
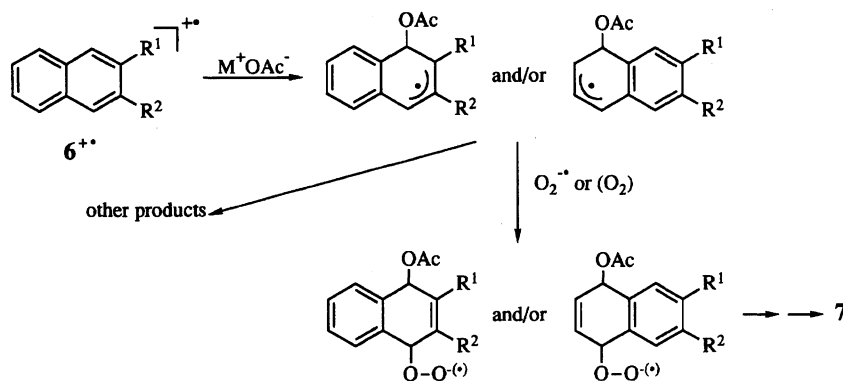
Scheme 5.

Experimental

¹H and ¹³C NMR spectra were taken on a Bruker AC-250P spectrometer for CDCl₃ solutions with tetramethylsilane used as an internal standard. IR spectra were taken on a JASCO A-302 spectrometer. The fluorescence spectra were taken on a Hitachi MPF-4. The fluorescence lifetimes of DCA and CA were measured on a Horiba NAES 550 by a single-photon counting method. GLC and HPLC analyses were carried out on a Shimadzu GC-14A using a capillary column (CBP1-M25-025) and a JASCO HPLC system (875-UV, 860-CO, 880-PU, and an injector 7125), respectively.

Materials.   Substituted stilbenes (**1b**—**d**) were prepared by the Wittig reaction of benzylphosphonium chloride with substituted benzaldehydes.[11] Commercially available **1a**, **6a**—**c**, DCA, and CA were purified by recrystallization. All salts and 18-crown-6 ether were purchased and used without further purification. Acetonitrile was distilled from P₂O₅, and then from CaH₂.

Photooxygenation of Stilbenes (1).   Into a Pyrex vessel was introduced an acetonitrile solution (40 cm³) containing **1** (2 mmol), sensitizer (0.02 mmol), and the salt (4 mmol), and then was bubbled with oxygen. The solution was irradiated with an Eikosha PIH-300 high-pressure mer-

cury lamp through an aqueous CuSO₄/NH₃ filter solution. The analyses of **2**, **3**, **4**, and **5** were performed by GLC. The identification of **2a**—**d**, **3a**—**c** and **4** were performed by a direct comparison with an authentic sample in GLC analysis and NMR spectra. The authentic samples of **3a**—**c** were prepared by the reported methods.[17]

trans-2,3-Diphenyloxirane (**3a**): ¹H NMR δ=3.86 (2H, s) and 7.29—7.46 (10H, m); ¹³C NMR δ=62.82, 125.47, 128.30, 128.54, and 137.67.

trans-2-Phenyl-3-(4-methylphenyl)oxirane (**3b**): ¹H NMR δ=2.37 (3H, s), 3.85 (2H, d, J=4.2 Hz), 7.12—7.25 (4H, m), and 7.32—7.41 (5H, m); ¹³C NMR δ=21.24, 62.78, 62.89, 125.45, 128.25, 128.54, 129.25, 134.07, 137.20, and 137.18.

trans-2-Phenyl-3-(4-methoxyphenyl)oxirane (**3c**): ¹H NMR δ=3.67 (3H, s), 4.99 (1H, d, J=7.5 Hz), 6.04 (1H, d, J=7.5 Hz), and 7.06—7.33 (9H, m); ¹³C NMR δ=55.08, 76.60, 80.63, 113.67, 127.15, 128.10, 128.63, 129.64, 130.01, 134.44, and 139.16.

1-Acetoxy-1,2-diphenylethene (**5a**): ¹H NMR δ=2.21 (3H, s), 6.86 (3H, s), 7.37—7.52 (8H, m), and 7.94 (2H, d, J=8.3 Hz); ¹³C NMR δ=20.81, 128.65, 128.72, 128.81, 128.71, 129.17, 129.37, 130.00, 130.31, 133.53, 133.53, 134.49, and 170.52.

One isomer of 1-acetoxy-2-(4-methylphenyl)-1-phenyl-

ethene (**5b**): ^{13}CNMR $\delta = 20.83$, 21.68, 128.60, 128.68, 128.92, 129.10, 129.29, 129.33, 131.91, 133.43, 133.79, 134.50, and 170.50.

One isomer of 1-acetoxy-2-(4-methoxyphenyl)-1-phenylethene (**5c**): ^{13}CNMR $\delta = 20.85$, 55.45, 113.86, 128.47, 128.64, 129.11, 129.25, 130.16, 131.19, 132.10, 134.01, 163.74, and 170.57. The adduct (**5c**) from the photooxygenation of **1c** was isolated as a mixture of *trans* and *cis* isomer, but it was confirmed that the adduct was not 1-acetoxy-1-(4-methoxyphenyl)-2-phenylethene (**5c′**), which was prepared from the reaction of **1c** (5 mmol) with acetic acid (60 ml) in the presence of $Pd(OAc)_2$ (5 mmol), $Cu(OAc)_2$ (5 mmol), and LiCl (5 mmol) at 70°C.[18]

One isomer of **5c′**: ^{13}CNMR $\delta = 20.99$, 55.13, 113.57, 127.56, 127.56, 128.04, 128.19, 128.32, 128.85, 129.35, 129.93, 159.45, and 169.89.

Photooxygenation of Naphthalene Derivatives (6).
An O_2 saturated acetonitrile solution (40 cm³) containing **6**, DCA (0.04 mmol), and the salt (4 mmol) was irradiated in a similar way as in the case of **1**. Product analyses were carried out on HPLC. The identification of **7a**, **7c**, **8**, and **9** was performed by direct comparisons with commercially available authentic samples. Dimethyl ester of **7b**: ^{1}HNMR $\delta = 2.30$ (3H, s), 3.85 (6H, s), and 7.41 (2H, s); IR (CHCl₃) 1720 cm⁻¹ (CO).

References

1) S. L. Mattes and S. Farid, "Organic Photochemistry," ed by A. Padwa, Marcel Dekker Inc., New York (1983), Vol. 6, p. 293.

2) C. Pac and O. Ishitani, *Photochem. Photobiol.*, **48**, 767 (1988); J. Santamaria, "Photoinduced Electron Transfer," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988), Part B, Chap. 3, p. 483.

3) K. Mizuno, N. Ichinose, T. Tamai, and Y. Otsuji, *Tetrahedron Lett.*, **26**, 5823 (1985); K. Mizuno, N.

Kamiyama, N. Ichinose, and Y. Otsuji, *Tetrahedron*, **41**, 2207 (1985); T. Tamai, K. Mizuno, I. Hashida, and Y. Otsuji, *Photochem. Photobiol.*, **54**, 23 (1991).

4) M. Yasuda, Y. Matsuzaki, T. Yamashita, and K. Shima, *Chem. Lett.*, **1989**, 551; M. Yasuda, Y. Matsuzaki, T. Yamashita, and K. Shima, *Nippon Kagaku Kaishi*, **1989**, 1292.

5) T. Yamashita, T. Tsurusako, M. Yasuda, and K. Shima, *Chem. Lett.*, **1991**, 1487.

6) J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 6083 (1980); R. C. Kanner and C. S. Foote, *J. Am. Chem. Soc.*, **114**, 678 (1992); R. C. Kanner and C. S. Foote, *J. Am. Chem. Soc.*, **114**, 682 (1992).

7) Santamaria reported that **8** was obtained from DCA-sensitized oxygenation of **6a** in the absence of salt in CH_2Cl_2; see Ref. 8.

8) J. Santamaria, P. Gabillet, and L. Bokobza, *Tetrahedron Lett.*, **25**, 2139 (1984); L.Bokobza and J. Santamaria, *J. Chem. Soc., Perkin Trans. 2*, **1985**, 269.

9) J. Eriksen, C. S. Foote, and T. L. Parker, *J. Am. Chem. Soc.*, **99**, 6456 (1977).

10) S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, **104**, 1454 (1982).

11) M. Yasuda, T. Isami, J. Kubo, M. Mizutani, T. Yamashita, and K. Shima, *J. Org. Chem.*, **57**, 1351 (1992).

12) E. I. Heiba, R. M. Desssau, and W. J. Koehl, Jr, *J. Am. Chem. Soc.*, **91**, 138 (1969).

13) I. Saito, K. Tamoto, and T. Matsuura, *Tetrahedron Lett.*, **31**, 2889 (1979); J. Santamaria, *Tetrahedron Lett.*, **22**, 4511 (1981); A. Albini and S. Spreti, *Z. Naturforsch., B*, **41b**, 1286 (1986).

14) M. Yasuda, C. Pac, and H. Sakurai, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 746.

15) M. Yasuda, C. Pac, and H. Sakurai, *J. Org. Chem.*, **46**, 788 (1981).

16) M. Yasuda, T. Yamashita, K. Shima, and C. Pac, *J. Org. Chem.*, **52**, 753 (1987); M. Yasuda, Y. Matsuzaki, K. Shima, and C. Pac, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 745.

17) S. W. May, S. L. Gorden, and M. S. Steltenkamp, *J. Am. Chem. Soc.*, **99**, 2017 (1977).

18) W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **88**, 2054 (1966).