© *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***62***, *96—101 (1989)* [Vol. 62, No. 1

Organic Photochemical Reactions. XXXI.[1] Photosensitized Ring-Cleavage Reactions of 2,2-Diaryloxetanes by Aromatic Nitriles

Kenichi NAKABAYASHI, Jun-ichi KOJIMA, Kimiko TANABE, Masahide YASUDA,
and Kensuke SHIMA*
Department of Industrial Chemistry, Faculty of Engineering, Miyazaki University,
Gakuen-Kibanadai, Miyazaki 889-21
(Received June 13, 1988)

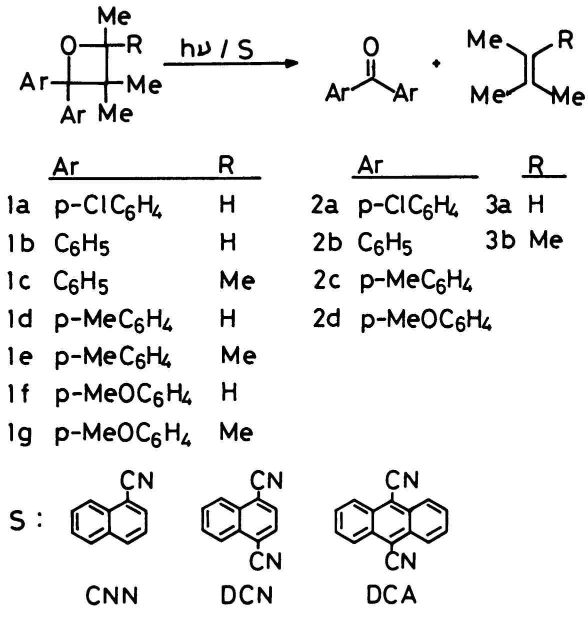
Photosensitized reactions of 2,2-diaryloxetanes by 1,4-dicyanonaphthalene, 1-cyanonaphthalene, and 9,10-dicyanoanthracene, which give such ring-cleavage products as substituted benzophenones and alkenes, have been investigated. Quantum yields for the ring cleavage vary with the substituents on both the aryl group and oxetane ring. The quantum yield increases with increase in electron-donating ability of the oxetane. The limiting quantum yields in the case of 1,4-dicyanonaphthalene-photosensitized reaction of 2,2-di-*p*-tolyl- or 2,2-bis(*p*-methoxyphenyl)-3,3,4-trimethyloxetane exceed unity. The mechanism is discussed in terms of electron transfer from oxetanes to the excited singlet state of the sensitizer as well as the regeneration process of the oxetane cation radical involving the hole transfer from substituted benzophenone cation radicals to oxetanes in the chain process.

Cleavage of oxetane into carbonyl–olefin pairs is well-known to occur by the treatment with Brφnsted acid or metal ion as well as by pyrolysis.[2] In these studies, the regio- and stereochemical control has been an interesting subject. On the other hand, photosensitized ring-cleavage reactions of such small ring compounds as cyclopropanes,[3] cyclobutanes,[4] oxiranes,[5] and aziridines[6] have received much attention from mechanistic and synthetic points of view. However, no photosensitized reactions of oxetanes have been reported. In order to develop the study of regioselective and efficient cleavage reactions of oxetanes, we attempted the ring cleavage of some 2,2-diaryloxetanes by photosensitization with such typical electron acceptor (S) as 1,4-dicyanonaphthalene (DCN), 1-cyanonaphthalene (CNN), and 9,10-dicyanoanthracene (DCA).

Results

Photoreaction. Photoreactions of 2,2-diaryloxetanes (**1a**—**h**) were carried out by irradiation of acetonitrile solutions at 313 nm for DCN and CNN runs and at 366 nm for DCA run, and the progress of the photoreactions was followed by gas chromatography. The photoproducts are shown in Scheme 1.

Pairs of substituted benzophenone (**2**) and alkenes (**3**) were formed by photosensitized reaction of **1a**—**h** with DCN. Such other products as 1,1-diaryl-2,2-dimethylethylene were not observed. The chemical yields of **2** and **3** in the photosensitized reaction with DCN are shown in Table 1. The formation of **2** occurred quantitatively whereas the yields of **3** were rela-



Scheme 1.

Table 1. Photosensitized Ring-Cleavage Reactions of Oxetanes (**1a**—**f**) with DCN[a]

Oxetane	Irradn time/h	Products (Yield/%)[b]	Conv. of **1**/%	Recov. of DCN/%
1a	24	**2a** (19) **3a** (11)	20	100
1b	20	**2b** (27) **3a** (20)	32	60
1c	24	**2b** (31) **3b** (24)	35	61
1d	10	**2c** (55) **3a** (55)	61	71
1e	25	**2c** (41) **3b** (17)	43	5
1f	4	**2d** (80) **3a** (71)	82	80

a) For acetonitrile solution (4 cm^3) containing **1** [0.05 mol dm^{-3}] and DCN [0.02 mol dm^{-3}]. b) GLC yields based on **1** used.

tively low in some cases except for the cases of **1d** and **1f**. DCN was recovered almost quantitatively except for the case of **1e** in which remarkable consumption of DCN was observed. Similarly, the photosensitized reaction of **1d** and **1f** with CNN or DCA proceeded to give **2** and **3** whereas no photosensitized reaction of **1a**—**c** with CNN or DCA occurred. The photosensitized reaction of **1f** with DCN and CNN did not proceed at all in less polar solvents such as benzene, dibutyl ether, dioxane, and tetrahydrofuran (THF) but proceeded slightly in ethyl acetate, 2-propanol, ethanol, and methanol. Acetonitrile was a better solvent for the occurrence of the efficient photoreactions. Moreover, it was confirmed that no reaction occurred at all in the dark or even upon direct irradiation of **1**.

Quantum Yields. The formation of **2** and **3** increased linearly with irradiation time up to 5% conversion. Limiting quantum yields were determined for the formation of **2** and **3** by the usual double-reciprocal plots of quantum yields (ϕ) vs. concentration of **1**. Figure 1 shows linear plots for the formation of **2** from DCN-photosensitized reaction of **1a**—**c**,**e**,**g**. Although such linear plots were also obtained from the formation of **3**, the slopes were steeper than those obtained from the formation of **2**, since the yields of **3** were lower than those of **2**. Such linear plots were not observed for the formation of **3b** from **1g**. Table 2 lists the intercept (I) and intercept-to-slope ratios (I/S) of the plots together with the limiting quantum yields for the formation of **2** and **3**. In the case of CNN and

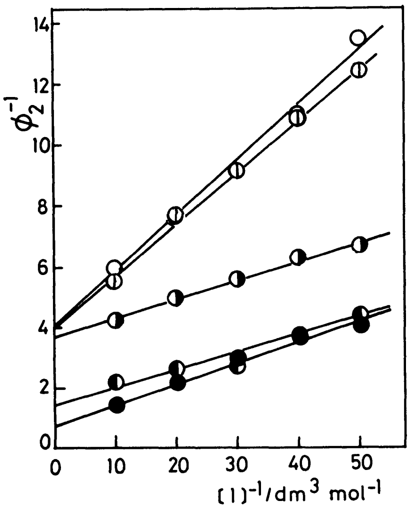


Fig. 1. Double-reciprocal plots of quantum yield for **2** formation vs. concentration of **1**: **1a** (-○-), **1b** (-⦶-), **1c** (-◑-), **1e** (-◐-), and **1g** (-●-).

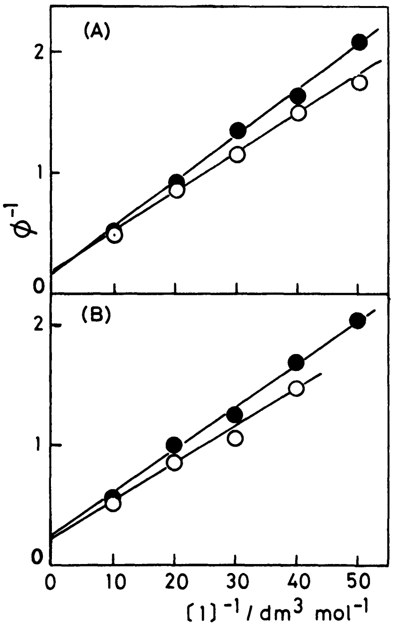


Fig. 2. Double-reciprocal plots of quantum yield for **2** (-○-) or **3a** (-●-) formation vs. concentration of **1**: (A) the case of DCN-**1d**, (B) the case of DCN-**1f**.

Table 2. Limiting Quantum Yields (ϕ) for the Formation of **2** and **3** and Fluorescence Quenching Rate Constants (k_q)

S (τ/ns)[a]	**1**	I[b]	I/S[b]	ϕ_2	ϕ_3	K_{SV}	k_q
						dm^3 mol^{-1}	dm^3 mol^{-1} s^{-1}
DCN (9.5)	**1a**	3.9	21	0.26	0.21	33	3.5×10^9
	1b	4.1	24	0.25	0.23	44	4.6×10^9
	1c	3.7	58	0.27	0.25	56	5.9×10^9
	1d	0.20	6.3	5.0	5.2	79	8.3×10^9
	1e	1.5	27	0.68	0.47	90	9.5×10^9
	1f	0.22	7.1	4.7	4.3	161	1.7×10^{10}
	1g	0.88	13	1.1	—[c]	144	1.5×10^{10}
CNN (9.3, 12.3[d])	**1d**			0.02[e]		4	0.4×10^9
	1f			0.40[e]		146	1.6×10^{10}
	1f					161[d]	1.3×10^{10}[d]
DCA (15.3)	**1d**			0.03[f]		20	1.3×10^9
	1f			0.10[f]		182	1.2×10^{10}

a) Fluorescence lifetimes. b) The intercept (I) and the intercept-to-slope ratios (I/S) of the plots for the formation of **2** in Figs. 1 and 2. c) Not determined. d) In benzene. e) For the acetonitrile solution containing **1** [0.05 mol dm^{-3}] and CNN [0.01 mol dm^{-3}]. f) For the acetonitrile solutions containing **1** [0.05 mol dm^{-3}] and DCA [1×10^{-4} mol dm^{-3}].

DCA, the observed quantum yields at [**1**]=0.05 mol dm^{-3} are shown in Table 2. It should be noted that the limiting quantum yields for the formation of **2** and **3** from DCN-photosensitized reaction of **1d** or **1f** were more than unity as is shown in Fig. 2.

The quantum yields were measured for DCN-photosensitized reaction of **1d** in the presence of various concentrations of methanol and the plots of ϕ for the formation of **2** and **3** vs. [MeOH] are shown in Fig. 3. The ϕ_2 decreased to 0.38 when more than 0.4 mol dm^{-3} of methanol was added and ϕ_3 gradually decreased with increase of concentration of methanol.

Fluorescence Quenching. The fluorescence of aromatic nitriles was quenched by oxetanes following linear Stern-Volmer relationships (Eq. 1). Table 2 includes the Stern-Volmer constants (K_{SV}) and the fluorescence quenching rate constants (k_q) calculated from K_{SV} and the fluorescence life time (τ).[7–9]

$$I_F^0/I_F = 1 + K_{SV}[\mathbf{1}] = 1 + k_q\tau[\mathbf{1}] \qquad (1)$$

Mass Spectrometry. The fragmentation of **1b**—**h** was studied by mass spectrometry at 70 eV. The relative intensities of the fragments are listed in Table 3 according to the fragmentation mode of Scheme 2 reported by Jones and McDonnell.[10]

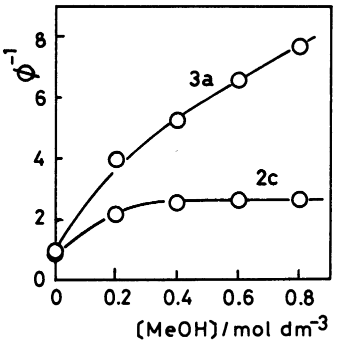
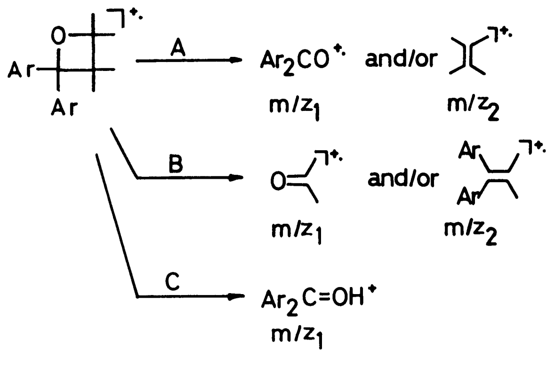


Fig. 3. Plots of the reciprocals of quantum yield for **2c** and **3a** vs. the concentration of methanol in DCN-photosensitized reaction of **1d**.



Scheme 2.

Table 3. Mass Spectral Data of Oxetanes (**1b**—**h**)[a]

Oxetane	Mode[b]	m/z_1	m/z_2	% Rel. Abundance[c]
1b	A	182 (12)[d]	70 (19)[e]	31
	B	44 (0)	208 (50)[f]	50
	C	183 (19)		19
1c	A	182 (6)[d]	84 (38)[g]	44
	B	58 (2)	208 (33)[f]	35
	C	183 (21)		21
1d	A	210 (11)[h]	70 (4)[e]	15
	B	44 (0)	236 (74)[i]	74
	C	211 (11)		11
1e	A	210 (8)[h]	84 (22)[g]	30
	B	58 (0)	236 (51)[i]	51
	C	211 (19)		19
1f	A	242 (11)[j]	70 (1)[e]	12
	B	44 (0)	268 (85)[k]	85
	C	243 (3)		3
1g	A	242 (11)[j]	84 (9)[g]	20
	B	58 (7)	268 (66)[k]	73
	C	243 (7)		7
1h	A	182 (47)[d]	56 (5)[l]	52
	B	44 (0)	194 (8)[m]	8
	C	183 (40)		40

a) % Relative abundance in parenthesis. b) Refers to Scheme 2. c) Sums of % relative abundance according to the mode. d) Includes relative intensity of m/z 105 (182—Ph). e) Includes relative intensity of m/z 55 (70—Me). f) Includes relative intensities of m/z 193 (208—Me) and 131 (208—Ph). g) Includes relative intensity of m/z 69 (84—Me). h) Includes relative intensity of m/z 119 (210—MeC$_6$H$_4$). i) Includes relative intensities of m/z 221 (236—Me) and 145 (236—MeC$_6$H$_4$). j) Includes relative intensity of m/z 135 (242—MeOC$_6$H$_4$). k) Includes relative intensities of m/z 253 (268—Me) and 161 (268—MeOC$_6$H$_4$). l) Includes relative intensity of m/z 41 (56—Me). m) Includes relative intensities of m/z 179 (194—Me) and 117 (194—Ph).

Discussion

Mechanism. There is no doubt that the photosensitization proceeds via the excited singlet state of aromatic nitriles since the rate constants for the fluorescence quenching of DCN by **1a**—**g** as well as the fluorescence quenching of DCA or CNN by **1f** are close to the diffusion-controlled rate in acetonitrile (2×10^{10} dm^3 mol^{-1} s^{-1}).[11] Moreover the intercept-to-slope ratio (I/S) obtained from quantum yield measurements shows reasonable agreement with the K_{SV} values for the fluorescence quenching in the case of DCN-**1a**—**c**. Table 4 lists the calculated free energy changes for the electron-transfer process from oxetanes to the excited singlet state of aromatic nitriles (^{1}S*) using the Rehm–Weller equation.[4,11] The calculated values for DCN-**1a**—**f** or DCA- and CNN-**1f** pairs are substantially negative. Therefore, it is strongly suggested that the electron transfer from oxetanes to ^{1}S* is responsible for the initiation process of photosensitized ring-cleavage reactions as reported for the photoreactions of some benzene derivatives with aromatic nitriles.[12] However, no photosensitized ring-cleavage reaction of **1f** with DCN or CNN in less polar solvents occur at all, though the fluorescence of S is efficiently quenched by **1f** in these solvents. From the above results, the cleavage of oxetane ring is suggested to proceed via the oxetane cation radical ($1^{+\cdot}$) formed by the complete electron transfer from oxetanes to ^{1}S* rather than via exciplex formation. Consequently, mechanistic pathways for the photosensitized reaction with S are shown in Scheme 3. A usual kinetic treatment gives Eq. 2.

$$\phi^{-1} = \frac{1}{\alpha\beta}\left(1 + \frac{1}{k_A\tau[1]}\right) \tag{2}$$

Since the oxidation potentials of 2,2-diaryloxetanes are similar to those of the corresponding benzene derivatives,[13] the positive charge in the photogenerated cation radicals of oxetanes is suggested to develop over the aryl groups. Therefore, the ring cleavage of $1^{+\cdot}$ should be induced by the decrease of electron density in the C_2–C_3 σ bond through σ–π interaction between the aryl groups and the C_2–C_3 bond of the oxetane ring (Scheme 4). DCN-photosensitized reaction of *cis*-3,4-dimethyl-2,2-diphenyloxetane (**1h**) gave the mixture of *cis*- and *trans*-2-butene (**3c**) in 1:4—5 ratio and **2b** (Scheme 5). Such nonstereospecific cleavage of the oxetane ring arose from the stepwise bond-fission at C_2–C_3 of oxetane ring followed by free rotation around the C_3–C_4 bond. An alternative isomerization mechanism via the cation radical of **3c** is unlikely to operate in the photosensitized reaction of **1h**, since mass spectra of **1h** show that $\mathbf{3c}^{+\cdot}$ is scarcely produced from the fragmentation of $\mathbf{1h}^{+\cdot}$. Thus $\mathbf{2}^{+\cdot}$ and/or $\mathbf{3}^{+\cdot}$ are formed by the cleavage of the ring-opened cation radical and reduced with anion radical of S ($S^{\cdot-}$) to give **2** and **3**. The formation of $\mathbf{2}^{+\cdot}$ and/or $\mathbf{3}^{+\cdot}$ are also suggested by the fact that the quantum yields for the

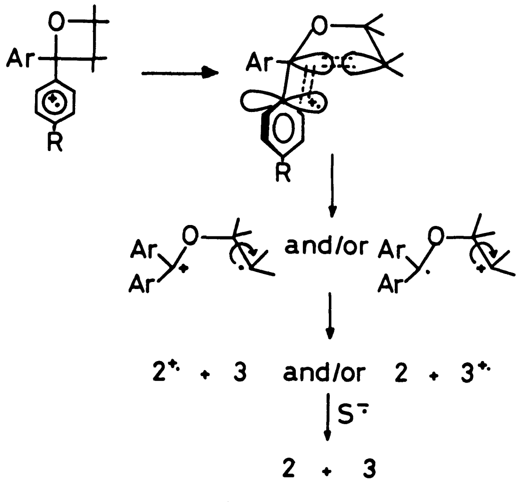
$$\begin{aligned}
&S \xrightarrow{h\nu} {}^1S^* \\
&{}^1S^* \xrightarrow{1/\tau} S \\
&{}^1S^* + 1 \xrightarrow{a k_A} S^{\cdot-} + 1^{+\cdot} \\
&{}^1S^* + 1 \xrightarrow{(1-a)k_A} S + 1 \\
&1^{+\cdot} \xrightarrow[S^{\cdot-}]{\beta} 2 + 3 \\
&1^{+\cdot} \xrightarrow{1-\beta} 1 \text{ and/or others}
\end{aligned}$$

Scheme 3.

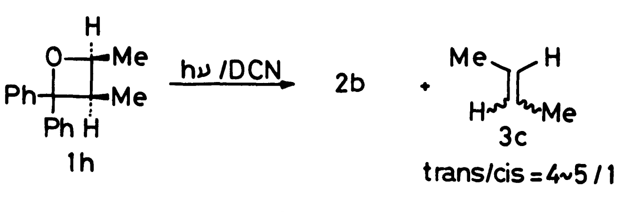
Table 4. Oxidation Potentials ($E^{ox}_{1/2}$) of **1a**—**f** and Calculated Free Energy Changes (ΔG) for Electron Transfer from **1a**—**f** to ^{1}S*

Oxetane	$E^{ox}_{1/2}$/V[a]	ΔG/kJ mol^{-1}[b]		
		DCN	CNN	DCA
1a	2.05	−39	55	23
1b	1.97	−47	48	15
1c	2.02	−42	52	19
1d	1.80	−63	31	−2
1f	1.44	−98	−3	−36

a) Half-wave oxidation potential vs. Ag/AgNO$_3$ in acetonitrile. b) Calculated values using the Rehm–Weller equation: see Refs. 4 and 11.



Scheme 4.



Scheme 5.

formation of **2** and **3** were diminished by the nucleophilic reaction of methanol in DCN-photosensitization of **1d** as shown in Fig. 3.

Consideration of Chain Mechanism. The chain mechanism should be taken into account in the case of **1d** and **1f** since the limiting quantum yields obtained from Fig. 2 exceed unity. The $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$ generated from the cleavage of the oxetane cation radical are candidates for the chain carrier in the regeneration process of oxetane cation radicals. The hole transfer from $\mathbf{3}^{+\cdot}$ to oxetanes is disadvantageous since the oxidation potentials of **3** are much lower than those of oxetanes showing that the hole-transfer process is substantially endothermic ($E^{\text{ox}}_{1/2}$=1.47 V for **3a** and 1.13 V for **3b**).[7] The hole transfer from $\mathbf{2}^{+\cdot}$ to oxetane is conceivable for the regeneration pathways of $\mathbf{1}^{+\cdot}$. Therefore, the reaction mechanism for DCN-photosensitization of **1d** and **1f** should include Eq. 3 in addition to Scheme 3. The I/S values for the chain process are much smaller than the K_{SV} values in Table 2. DCN-photosensitization of **1e** and **1g** in which I/S values are smaller than the K_{SV} values might proceed by a mechanism involving a chain mechanism.

$$\mathbf{2}^{+\cdot} + \mathbf{1} \longrightarrow \mathbf{2} + \mathbf{1}^{+\cdot} \qquad (3)$$

Jones and McDonnell reported that the fragmentation of the oxetane ring in mass spectra occurred according to the modes A, B, and C as is shown in Scheme 2.[10] Though the mass spectrometry features are different from those of photosensitized reactions, we can estimate the ratio of $\mathbf{2}^{+\cdot}$ to $\mathbf{3}^{+\cdot}$ generated from $\mathbf{1}^{+\cdot}$ by the fragment intensity of mass spectra in mode A as shown in Table 3. It was found that the ratio of $\mathbf{2}^{+\cdot}$ to $\mathbf{3}^{+\cdot}$ in the case of **1d** and **1f** was greater than in the other cases. In other words, it is shown that the fragmentation of $\mathbf{1}^{+\cdot}$ gives a pair of $\mathbf{2}^{+\cdot}$ and **3** more than a pair of **2** and $\mathbf{3}^{+\cdot}$ in the case of **1d** and **1f** in which the limiting quantum yield exceeds unity. Therefore, it is again indicated that $\mathbf{2}^{+\cdot}$ plays an important role in the chain process.

In conclusion, the regioselective ring-cleavage reaction of oxetanes was accomplished by photosensitization with aromatic nitriles. The regioselectivity was caused by selective C_2–C_3 bond-fission of the oxetane cation radicals generated by photochemical electron transfer. Moreover, the reaction efficiencies were determined by the electron-donating abilities of oxetanes as well as by occurrence of chain processes.

Experimental

Instruments. Gas chromatography was performed on a Shimadzu GC-8A gas chromatograph using a 50 cm column of 2% OV-1 or 2% OV-17 on Chromosorb W for analyses of **1a—h**, **2a—d**, and DCN, a 3 m column of DC-550 on Uniport B for analyses of **3a**, a 1 m column of PEG-20M for analyses of **3b**, and a 2 m column of Unipak S (Gasukuro Kogyo) for analyses of **3c**. IR and ^{1}H NMR spectra were obtained on a Hitachi 260-50 spectrometer and a JEOL JNM60 spectrometer, respectively. The fluorescence quenching experiments were performed for degassed acetonitrile or benzene solutions (3 cm^3) containing DCN (1$\times$10^{-3} mol dm^{-3}), CNN (1$\times$10^{-3} mol dm^{-3}), or DCA (2$\times$10^{-5} mol dm^{-3}) on a Hitachi MPF-4 spectrometer. Oxidation potentials of **1a—d, f** were determined by a Yanagimoto V10-PG cyclic voltammeter vs. Ag/AgNO$_3$ in acetonitrile using tetraethylammonium tetrafluoroborate as the supporting electrolyte.[14] Mass spectra were measured on a JEOL D-300S equipped with a JMA 2000 data analyzer.

Materials. Commercial 1-cyanonaphthalene was purified by the method described in a previous paper.[7] 9,10-Dicyanoanthracene was purified by repeated recrystallization from benzene. 1,4-Dicyanobenzene was prepared according to the literature method[15] and was purified by repeated recrystallization from benzene. The preparation of oxetanes was carried out by the irradiation of a benzene solution containing the substituted benzophenone and the alkene by high-pressure Hg lamp according to the procedure described in the literature.[16] The purification of the oxetanes was performed by column chromatography on silica gel and then by repeated recrystallization from methanol. Some data of oxetanes (**1a—f**) are as follows: **1a**, 80% of yield, mp 71—72 °C, ^{1}H NMR (CCl$_4$) δ=1.07 (s, 6H), 1.28 (d, 3H, J=6 Hz), 4.43 (q, 1H, J=6 Hz), 7.07—7.44 (m, 8H). **1b**, 88%, mp 104.5—105.5 °C, ^{1}H NMR (CCl$_4$) δ=0.98 (s, 6H), 1.18 (d, 3H, J=6 Hz), 2.17 (q, 1H, J=6 Hz), 6.92—7.43 (m, 10H). **1c**, 82%, mp 121.5—122 °C, ^{1}H NMR (CCl$_4$) δ=1.10 (s, 6H), 1.27 (s, 6H), 7.08—7.59 (m, 10H). **1d**, 77%, mp 99—100 °C, ^{1}H NMR (CCl$_4$) δ=0.95 (s, 6H), 1.15 (d, 3H, J=6 Hz), 4.34 (q, 1H, J=6 Hz), 6.79—7.30 (m, 8H). **1e**, 90%, mp 117—118 °C, ^{1}H NMR (CCl$_4$) δ=1.0 (s, 6H), 1.23 (s, 6H), 2.18 (s, 3H), 6.9 (d, J=8 Hz, 4H), 7.27 (d, J=8 Hz, 4H). **1f**, 87%, mp 91.5—92 °C, ^{1}H NMR (CCl$_4$) δ=0.97 (s, 6H), 1.20 (d, 3H, J=6 Hz), 4.40 (q, 1H, J=6 Hz), 6.55—7.42 (m, 8H). **1g**, 31%, mp 92—93 °C, ^{1}H NMR (CCl$_4$) δ=1.0 (s, 6H), 1.2 (s, 6H), 3.6 (s, 6H), 6.7 (d, J=8 Hz, 4H), 7.3 (d, J=8 Hz, 4H). **1h**, 75%, mp 87—88 °C, ^{1}H NMR (CCl$_4$) δ=0.83 (d, J=6 Hz, 3H), 1.3 (d, J=6 Hz, 3H), 3.03 (d-q, J=6 Hz, 6 Hz, 1H), 4.26 (d-q, J=6 Hz, 6 Hz, 1H), 6.9—7.26 (m, 10H).

Photoreactions and Determination of Quantum Yields. Photoirradiation was carried out with an Eikosha PIH-300 high-pressure Hg lamp under cooling with water using appropriate light filters and a "merry-go-round" turntable. A potassium chromate solution (0.2 g dm^{-3}, 10 mm path length) was used to isolate the 313-nm light, whereas the 366-nm light was obtained by the passage through a glass filter (Corning CS7-37) and 10% HCl aqueous solution of BiCl$_3$ (6.67 g dm^{-3}, 10 mm path length). A 2-hexanone actinometer and a trioxalatoferrate(III) actinometer were used for the determination of the quantum yields at 313 nm for the CNN and DCN-photosensitized reaction and at 366 nm for the DCA runs respectively.[17] The concentrations of DCN, CNN, and DCA were set in 0.02, 0.01, and 1$\times$10^{-4} mol dm^{-3}, respectively. These were confirmed to be high enough for the complete absorption of the incident light during the photoreactions. Pyrex glass tubes (8 mm i.d.) were used as the common vessels for the photoreactions and actinometry.

The authors wish to thank Professor Chyongjin Pac, Osaka University, for his kind and helpful discussions. We also thank Professor Toshinori Kokubu, Miyakonojo National College of Technology, for measurement of the oxidation potentials. This work was supported by a Grand-in-Aid for Scientific Research, No. 62550616, from the Ministry of Education, Science and Culture.

References

1) Part XXX: K. Shima, K. Tanabe, S. Furukawa, J. Saito, and K. Shirahashi, *Bull. Chem. Soc. Jpn.*, **57**, 1515 (1984).

2) D. R. Arnold, "Advances in Photochemistry," ed by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., John Wiley and Sons, New York (1968), Vol. 6, p. 301; G. Jones, II, "Organic Photochemistry," ed by A. Padwa, Marcel Dekker, New York (1981), Vol. 5, p. 1.

3) K. Mizuno, J. Ogawa, and Y. Otsuji, *Chem. Lett.*, **1981**, 741; V. R. Rao and S. S. Hixson, *J. Am. Chem. Soc.*, **101**, 6458 (1979).

4) C. Pac, T. Ohtsuki, Y. Shiota, S. Yanagida, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **59**, 1133 (1986); C. Pac, *Pure Appl. Chem.*, **58**, 1249 (1986).

5) A. P. Schaap, S. Siddiqui, S. D. Gagnon, and L. Lopez, *J. Am. Chem. Soc.*, **105**, 5149 (1983); A. P. Schaap, L. Lopez, and S. D. Gagnon, *J. Am. Chem. Soc.*, **105**, 663 (1983).

6) A. P. Schaap, G. Prasad, and S. Siddiqui, *Tetrahedron Lett.*, **25**, 3035 (1984).

7) C. Pac, M. Yasuda, K. Shima, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **55**, 1605 (1982).

8) P. K. Das, A. J. Muller, and G. W. Griffin, *J. Org. Chem.*, **49**, 1977 (1984).

9) J. Eriksen and C. S. Foote, *J. Phys. Chem.*, **82**, 2659 (1978).

10) G. Jones, II and L. P. McDonnell, *Org. Mass Spectrom.*, **10**, 1 (1975); *Tetrahedron Lett.*, **1975**, 4633.

11) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

12) S. Farid, "Organic Photochemistry," ed by A. Padwa, Marcel Dekker, New York, Vol. 6, p. 233.

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

14) T. Majima, C. Pac, and H. Sakurai, *J. Am. Chem. Soc.*, **102**, 5265 (1980).

15) L. Heiss, E. F. Paulus, and H. Lehling, *Justus Liebigs Ann. Chem.*, **1980**, 1583.

16) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, **1964**, 1425.

17) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), p. 119.