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Photo-Cycloaddition Reactions of 2-Pyrones

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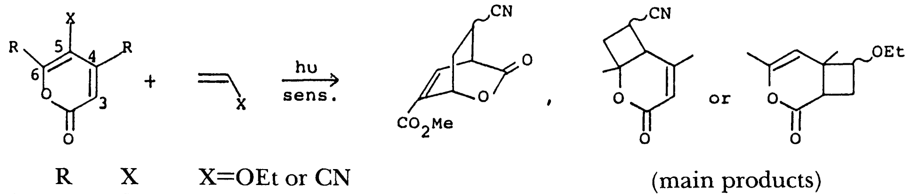
Sensitized photoreactions of two 2-pyrones with five unsaturated compounds were investigated. The reactions of 2-pyrones with electron-deficient ethylenes gave [4+2]cycloadducts (**3**) and [2+2]cycloadducts (**4**) across the C_5-C_6 double bonds in the 2-pyrones. On the other hand, reactions with an electron-donating ethylene, ethyl vinyl ether (**2i**), gave other kinds of [2+2]cycloadducts (**5**) and a [4+2]cycloadduct (**6**), site- and regio-selectively. These two kinds of reactions were inferred to start at the C-6 and C-4 positions of the 2-pyrones to give **3** or **4**, and **5** or **6**, respectively. The regioselectivity of **6** was opposite to that for a thermal [4+2]cycloadduct (**7**). The substituents on 2-pyrones also influenced the product-distribution and the triplet energy-level.

2-Pyrone (**1**) is a simple 2,4-pentadien-5-olide. Although much attention has been focused on thermal cycloaddition reactions,[1] the investigation of the photochemical ones has not been extended beyond our reports,[2-4] except for dimerizations.[5] Sensitized photoreactions of 4,6-dimethyl-2-pyrone (**1c**) with electron-deficient ethylenes gave mainly [2+2]cycloadducts across the C_5-C_6 double bond in **1c**,[2] while methyl 2-pyrone-5-carboxylate (**1a**) afforded [4+2]-cycloadducts under similar conditions, as shown in Sheme 1. The similar photoreactions of **1c** with chloroethylenes gave many kinds of cycloadducts. Some of them were also transformed into 5-ethynyl-2-pyrones etc. by dehydrochlorinations and valence isomerization.[6] Since **1** has a conjugated dienone system, photoadditions between a variety of ethylenes possess many possibilities regarding the addition type and stereochemistry.[7] The photoaddition reactions of 2-pyrones are interesting from both theoretical and synthetic respects. We now report on sensitized photoreactions of two 2-pyrones (**1b**, **1d**) with five kinds of unsaturated compounds (**2**). **1b** is ethyl 4,6-dimethyl-2-pyrone-5-carboxylate, and is thought to lie between **1a** and **1c** regarding the π-electronic properties of their diene moieties. **1d** is 4-methoxy-6-methyl-2-pyrone and the diene property may be slightly more electron-donating than that of **1c**.

Results and Discussion

Photochemical Products. The present photoadditions are as follows. The photoreactions of 2-pyrones **1b** or **1d** with **2e**, **2f**, **2g**, **2h**, or **2i** in Scheme 2 were carried out in the presence of benzophenone, as a sensitizer, in acetone solvent with a 400W high-pressure mercury lamp at −20—−10 °C or at room temperature. The product-separation methods were similar to those used in our previous studies and the chemical structures were elucidated through a spectral comparison with previous data concerning **1a** and **1c**.[2-4] The results are shown in Scheme 2 and Table 1. The steric structures of the products are shown in Schemes 3 to 5. Thus, **1b** gave an *exo*-[4+2]cycloadduct, **3bf** (54% yield), from a reaction with **2f**; an



	R	X
1a;	H	CO_2Me
1c;	Me	H

X=OEt or CN

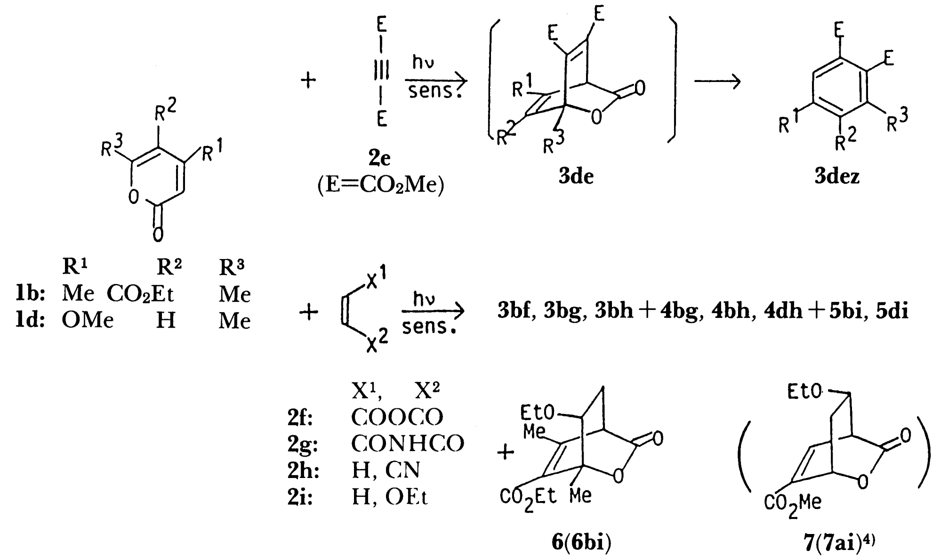
(main products)

Scheme 1.

Table 1. Results of Sensitized Photoaddition Reactions of 2-Pyrones

2-Pyrone	Unsaturated compound/Product(%)				
	2e	**2f**	**2g**	**2h**	**2i**
1b	—	**3bf**(54)	**3bg**(59)+**4bg**(19)	**3bh**(16)+**4bh**(61)	**5bi**(71)+**6bi**(9)
1d	**3dez**(35)[a]	No adduct	No adduct	**4dh**(46)	**5di**(21) **5di**(75)[b]

a) Subscript z means decarboxylation. b) GC data.



2e
(E=CO_2Me)

3de

3dez

	R^1	R^2	R^3
1b:	Me	CO_2Et	Me
1d:	OMe	H	Me

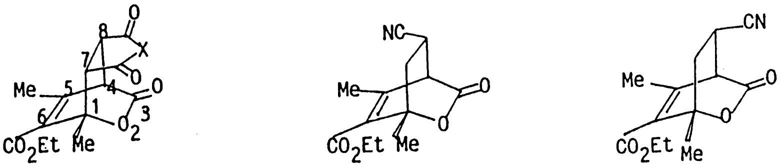
3bf, 3bg, 3bh + 4bg, 4bh, 4dh + 5bi, 5di

	X^1, X^2
2f:	COOCO
2g:	CONHCO
2h:	H, CN
2i:	H, OEt

6(6bi)

7(7ai)[4]

Scheme 2.



3bf: X=O
3bg: X=NH

3bhn

3bhx

Scheme 3.

4bg

	R^1	R^2	R^3
4bhn:	Me	CO_2Et	Me(endo)
4bhx:	Me	CO_2Et	Me(exo)
4dhn:	OMe	H	Me(endo)
4dhx:	OMe	H	Me(exo)

Scheme 4.

	R^1	R^2
5bin:	Me	CO_2Et
5din:	OMe	H

	R^1	R^2
5bix:	Me	CO_2Et
5dix:	OMe	H

Scheme 5.

exo-[4+2]cycloadduct, **3bg** (59%), and a [2+2]cycloadduct, **4bg** (19%), across the C_5-C_6 double bond with **2g**; a 8-cyano-[4+2]cycloadduct, **3bh** (16%), and two 7-cyano-[2+2]cycloadducts, **4bhn** (30%) and **4bhx** (31%), across the C_5-C_6 bond with **2h**; and an 7-ethoxy-[2+2]cycloadduct, **5bi** (71%), across the C_3-C_4 bond; and an 7-ethoxy-[4+2]cycloadduct, **6bi** (9%), with **2i**, respectively. The regiospecificity in the photo-[4+2]cycloadduct **6bi** was inverse to that for the thermal [4+2]cycloadduct, **7ai**,[3] obtained at ambient temperature.

On the other hand **1d** gave dimethyl 5-methoxy-3-methylphthalate (**3dez**, 35%) from a photoreaction with DMAD. **3dez** was deduced to be formed through a decarboxylation of the unstable [4+2]cycloadduct **3de** (Scheme 2).

The photoreaction of **1b** with **2f** at ambient temperature did not give [4+2]cycloadduct, **3bf**. [4+2]cycloadducts **3bg** and **3bh** foamed to decompose during the melting point determinations in a similar manner with **3bf**. The above-mentioned photoreactions using **1b** and **2e** were therefore carried out at low temperature, respectively. These [4+2]cycloadducts possibly have succesive cross-[4+2]cycloadducts with some dienophiles and cage-compounds, in a similar manner to [4+2]cycloadducts of **1c** with **2f**.[2]

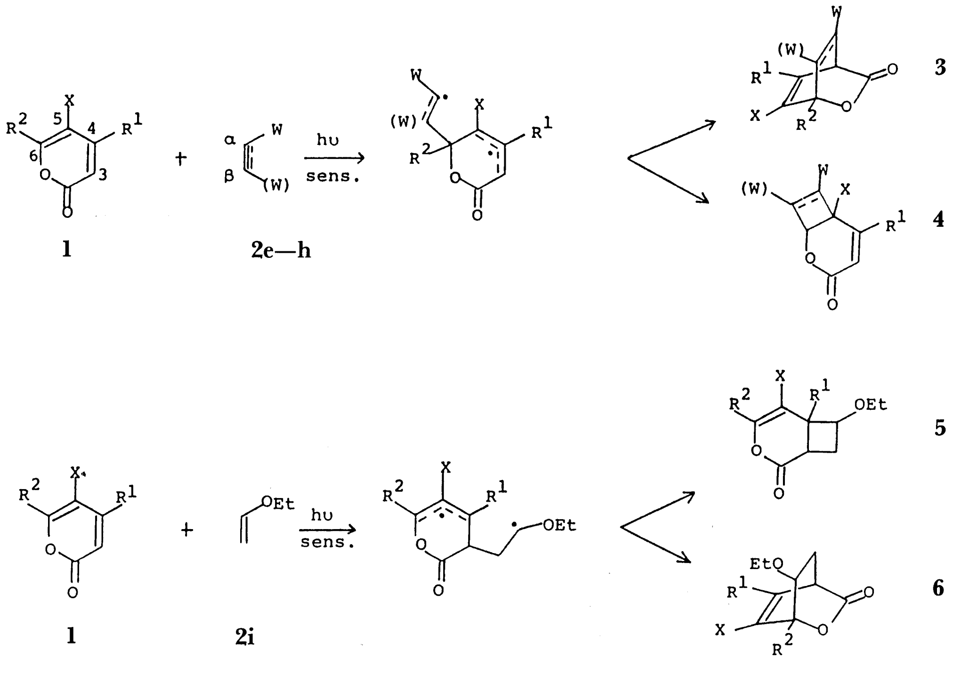
1d gave two [2+2]cycloadducts, **4dh** (46%), across the C_5-C_6 bond (*endo*- and *exo*-7-cyano isomers, **4dhn** and **4dhx**) with **2h**, and two [2+2]-cycloadducts, **5di** (21%), across the C_3-C_4 bond (*endo*- and *exo*-7-ethoxy isomers, **5din** and **5dix**) with **2i**, respectively. In the structure elucidations of these isomers, their ^{1}H NMR data were effective,[2–4] as detailed in the Experimental Section. Namely, the data included magnetic anisotropy due to the double bonds in the *exo*-isomers and/or long-range spin-spin couplings in the 4-membered rings of the *exo*-isomers.

The Photoaddition Reactivity. In the sensitized photoreactions of 2-pyrones toward several ethylenes or DMAD (**2e**), there were four kinds of primary products: **3**, **4**, **5**, and **6**. The product distribution was inferred to mainly depend on the electronic properties of the two substrates. Thus, a decrease in the electron-donating property of the substituents on the two substrates, **1** and **2** (left to right, and high to low in Table 1), changed the product-distribution as follows:

$$\mathbf{3} \rightarrow \mathbf{3}+\mathbf{4} \rightarrow \mathbf{4} \rightarrow \mathbf{5}+\mathbf{6}\ \text{(minor)}.$$

Since they were also regioselective and sensitized products, the addition reactions were inferred to proceed in the two stepwise paths shown in Scheme 6.

We next describe the triplet energies and the reactions of **1b**, **1d**, and maleic anhydride (**2f**) concerning the "no adduct" results with these substrates given in Table 1. The reaction results of **1b** with **2f** in the presence of various sensitizers are shown in Fig. 1. Product **3bf** was afforded only with sensitizers possessing the triplet energies over 56 kcal mol^{-1}. Similar results for **1d** with **2h** are shown in Fig. 2. The cycloadduct **4dh** just occurred in the presence of sensitizers with triplet energies over 62 kcal mol^{-1}. This means that the lowest triplet energies of **1b** and **1d** are nearly 56 and 62 kcal mol^{-1}, respectively. The triplet energy of **2f** has been estimated to be 72 kcal mol^{-1} from the phosphorescence.[8] Though triplet-



Scheme 6.

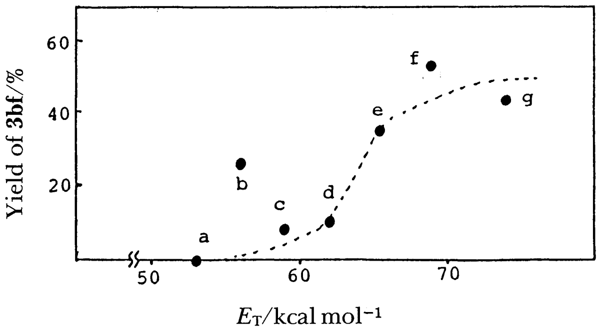


Fig. 1. Sensitization for photoadditions of **1b** by triplet sensitizers.
a; 9-Fluorenone, b; Biacetyl, c; 2-Acetonaphthone, d; Michler's ketone, e; Thioxanthone, f; Benzophenone, g; Acetophenone.

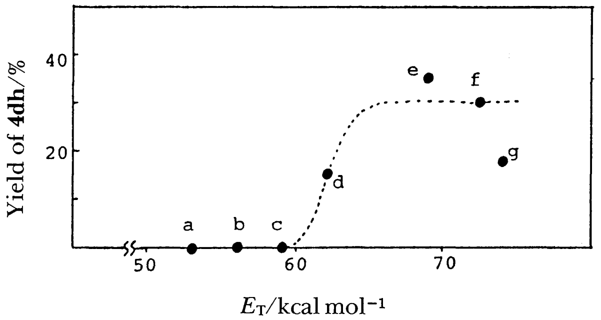


Fig. 2. Sensitization for photoadditions of **1d** by triplet sensitizers.
a; 9-Fluorenone, b; Biacetyl, c; 2-Acetonaphthone, d; Michler's ketone, e; Benzophenone, f; Xanthone, g; Acetophenone.

quenching of **1d** by **2f** may not have occurred according to these data, the triplet photoreaction of **1d** with **2f** did not occur. The reaction of **1d** with **2e** gave **3dez** via a photoadduct; that of **1c** with **2f** also gave a photo-[4+2]adduct.[2] It may be very difficult to understand the reason for the existence of "no adduct" between **1d** and **2f**. The diene moiety of **1d** may be more electron-rich than that of **1c**, and an electron-deficient olefin **2f** is so plain that it may be more effective than **2e** for overlapping between two molecules. Exciplex formation between **1d** and **2f** may more easily occur than those between **1c** and **2f**, and **1d** and **2e**. Exciplex quenchings appeared in the photoreactions between an α,β-unsaturated lactone and 1,1-dimethoxyethylene,[9] and between 2-pyridone and **1f**.[7] "No adduct" may also have been caused due to strong exciplex quenching between **1d** and **2f**. The reactivity in photoadditions of 2-pyrones is sensitive.

Experimental

General and Materials. All melting points were uncorrected. The IR spectra were determined with a JASCO A-3 spectrometer. The ^{1}H NMR spectra were measured on a JEOL JNM-MH-100 (100 MHz) spectrometer using TMS as the internal reference. The mass spectra were measured with a JEOL JMS-01SG spectrometer. All of the photoaddition reactions were monitored using a GC, performed at 170 °C (column temp) on a Yanagimoto G80 instrument using a column of Silicone SE-30 (10%)/Chromosorb W (AW). Wakogel C200 was used for preparative column chromatography.

Methyl 2-pyrone-5-carboxylate (**1a**),[10] ethyl 4,6-dimethyl-2-pyrone-5-carboxylate (**1b**),[11] 4,6-dimethyl-2-pyrone (**1c**),[11] and 4-methoxy-6-methyl-2-pyrone (**1d**)[12] were prepared according to methods previously described in the literature.

Low-Temperature Photoreaction of 1b with 2f. A solution of **1b** (3.0 g, 15 mmol), **2f** (2.9 g, 30 mmol), and benzophenone (1.0 g, 5.4 mmol) in 200 ml of acetone under nitrogen was irradiated with a Riko immersion-type 400W high-pressure mercury lamp through a Pyrex vessel at −10—−20 °C for 5 h. The solvent was removed and the residue cooled at 0 °C to give 2.42 g (54%) of **3bf**.

3bf: Colorless needles from acetone; mp 159—163 °C (decomp); IR (KBr) 1860, 1780, 1700 cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta=1.24$, 4.22 (CO$_2$Et), 1.84, 2.14 (each 3H, s, Me), 3.58 (1H, d, $J_{7,8}=10.0$ Hz, 7-H), 3.88 (1H, d, $J_{4,8}=3.8$ Hz, 4-H), 4.04 (1H, dd, $J_{4,8}=3.8$, $J_{7,8}=10.0$ Hz, 8-H); MS *m/z* 250 (M−CO$_2$ 15%), 132 (base peak).

Found: C, 56.83; H, 4.78%. Calcd for $C_{14}H_{14}O_7$: C, 57.14; H, 4.80%.

Low-Temperature Photoreaction of 1b with 2g. A solution of **1b** (3.0 g, 15 mmol), **2g** (1.25 g, 30 mmol), and benzophenone (1.0 g, 5.4 mmol) in 200 ml of acetone was irradiated for 1 h under the same conditions mentioned above; the solvent was then removed. The residue was chromatographed on a silica-gel column with benzene-acetone (10 : 1) to give 2.65 g (59%) of **3bg** and 0.87 g (19%) of **4bg**.

3bg: Colorless needles from ethyl acetate-acetone (5 : 1); mp 142—146 °C (decomp); IR (KBr) 1790, 1770, 1720 cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta=1.26$, 4.25 (CO$_2$Et), 1.82, 2.12 (each 3H, s, Me), 3.16 (1H, d, $J_{7,8}=9.5$ Hz, 7-H), 3.52 (1H, dd, $J_{4,8}=3.0$, $J_{7,8}=9.5$ Hz, 8-H), 3.72 (1H, d, $J_{4,8}=3.0$ Hz, 4-H), 11.55 (1H, s, NH); MS *m/z* 293 (M$^+$, 0.1%) 133 (base peak).

Found:C, 57.20; H, 5.16; N, 4.77%. Calcd for $C_{14}H_{15}NO_6$: C, 57.34; H, 5.16; N, 4.28%.

4bg: Colorless needles from ethyl acetate-acetone (5 : 1); mp 210—214 °C; IR (KBr) 1740, 1720 cm^{-1}; ^{1}H NMR (DMSO-d_6) $\delta=1.23$, 4.26 (CO$_2$Et), 1.52, 1.81 (each 3H, s, Me), 3.44, 3.87 (each 1H, d, $J_{7,8}=8.0$ Hz), 6.08 (1H, s, 4-H), 11.61 (1H, s, NH); MS *m/z* 293 (M$^+$, 2%), 196 (base peak).

Found: C, 57.38; H, 5.10; N, 4.78%. Calcd for $C_{14}H_{15}NO_6$: C, 57.34; H, 5.16; N, 4.78%.

Low-Temperature Photoreaction of 1b with 2h. A solution of **1b** (3.0 g, 15 mmol), **2h** (9.9 ml, 150 mmol), and benzophenone (1.0 g, 5.4 mmol) in 200 ml of acetone was irradiated for 1 h under the same conditions and the solvent removed. The residue was chromatographed with benzene-acetone (30 : 1) to afford 0.30 g (8%) of **3bhn** (*endo*-CN) and 1.18 g (31%) of **4bhn** (*endo*-CN). The continued elution with benzene-acetone (10 : 1) afforded 0.30 g (8%) of **3bhx** (*exo*-CN) and 1.14 g (30%) of **4bhx** (*exo*-CN).

3bhn: Colorless needles from diethyl ether; mp 118—121 °C (decomp); IR (KBr) 2250, 1755, 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) $\delta=1.34$, 4.28 (CO$_2$Et), 1.77, 2.26 (each 3H, s, Me), 2.06 (1H, dd, $J_{7endo,7exo}=13.0$, $J_{7endo,8}=4.0$ Hz, 7*endo*-H), 2.44 (1H, dd, $J_{7exo,7endo}=13.0$, $J_{7exo,8}=9.0$ Hz, 7*exo*-H), 3.30 (1H, ddd, $J_{8,7exo}=9.0$, $J_{8,7endo}=4.0$, $J_{8,4}=3.0$ Hz, 8-H), 3.63 (1H, d, $J_{4,8}=3.0$ Hz, 4-H); MS *m/z* 249 (M^+, 8%), 105 (base peak).

Found:C, 62.59; H, 6.06; N, 5.57%. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62%.

3bhx: Colorless needles from diethyl ether; mp 103—106 °C (decomp); IR (KBr) 2250, 1750, 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32, 4.28 (CO_2Et), 1.77, 2.14 (each 3H, s, Me), 2.29 (2H, d, $J_{7endo,8}=J_{7exo,8}=8.0$ Hz, 7*endo*-H, 7*exo*-H), 2.91 (1H, td, $J_{8,7exo}=J_{8,7endo}=8.0$, $J_{8,4}=2.5$ Hz, 8-H), 3.63 (1H, d, $J_{4,8}=2.5$ Hz, 4-H); MS *m/z* 250 (M^++1, 1%), 105 (base peak).

Found: C, 62.66; H, 6.08; N, 5.59%. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62%.

4bhn: Colorless oil; IR (neat) 2250, 1735, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30, 4.31 (CO_2Et), 1.47, 2.10 (each 3H, s, Me), 2.50 (1H, dd, $J_{8endo,8exo}=12$, $J_{8endo,7}=9.0$ Hz, 8*endo*-H), 2.67 (1H, dd, $J_{8exo,8endo}=12$, $J_{8exo,7}=10.0$ Hz, 8*exo*-H), 3.71 (1H, dd, $J_{7,8exo}=10.0$, $J_{7,8endo}=9.0$ Hz, 7-H), 6.21 (1H, bs, 4-H); MS *m/z* 249 (M^+, 2%), 196 (base peak).

Found: C, 62.23; H, 6.10; N, 5.48%. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62%.

4bhx: Colorless oil; IR (neat) 2250, 1735, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.33, 4.34 (CO_2Et), 1.78, 1.95 (each 3H, s, Me), 2.37 (1H, dd, $J_{8endo,8exo}=12.0$, $J_{8endo,7}=3.0$ Hz, 8*endo*-H), 2.82 (1H, dd, $J_{8exo,8endo}=12.0$, $J_{8exo,7}=11.0$ Hz, 8*exo*-H), 3.17 (1H, dd, $J_{7,8exo}=11.0$, $J_{7,8endo}=3.0$ Hz,7-H), 6.06 (1H, bs, 4-H): MS *m/z* 249 (M^+, 2%), 196 (base peak).

Found: C, 62.44; H, 6.08; N, 5.54%. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62%.

Low-Temperature Photoreaction of 1b with 2i. A solution of **1b** (3.0 g, 15 mmol), **2i** (14.4 ml, 150 mmol), and benzophenone (1.0 g, 5.4 mmol) in 200 ml of acetone was irradiated for 2 h; the solvent was then removed. The residue was chromatographed with benzene-acetone (30 : 1) to give 1.14 g (28%) of **5bin** (*endo*-OEt) and 1.76 g (43%) of **5bix** (*exo*-OEt). The continued elution with benzene-acetone (10 : 1) afforded 0.37 g (9%) of **6**.

5bin: Colorless oil; IR (neat) 1780, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20, 3.50 (OEt), 1.30, 4.22 (CO_2Et), 1.26, 2.24 (each 3H, s, Me), 2.22 (1H, ddd, $J_{8,8'}=12.0$, $J_{8',1}=10.5$, $J_{8,7}=3.0$ Hz, 8-H′), 2.54 (1H, ddd, $J_{8,8'}=12.0$, $J_{8',1}=8.0$, $J_{8',7}=7.0$ Hz, 8-H′), 3.12 (1H, ddd, $J_{1,8}=10.5$, $J_{1,7}=1.5$, $J_{1,8'}=8.0$ Hz, 1-H), 4.00 (1H, ddd, $J_{7,8'}=7.0$, $J_{7,1}=1.5$, $J_{7,8}=3.0$ Hz, 7-H); MS *m/z* 268 (M^+, 0.4%), 72 (base peak).

Found: C, 62.58; H, 7.47%. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51%.

5bix: Colorless oil; IR (neat) 1780, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.07, 3.42 (OEt), 1.32, 4.20 (CO_2Et), 1.58, 2.24 (each 3H, s, Me), 2.20 (1H, td, $J_{8,8'}=12.0$, $J_{8,1}=J_{8,7}=8.0$ Hz, 8-H), 2.50 (1H, t, $J_{1,8}=J_{1,8'}=8.0$ Hz, 1-H), 2.52 (1H, ddd, $J_{8,8'}=13.0$, $J_{8',1}=8.0$, $J_{8',7}=5.5$ Hz, 8-H′), 3.72 (1H, dd, $J_{7,8}=8.0$, $J_{7,8'}=5.5$ Hz, 7-H); MS *m/z* 268 (M^+, 1%), 72 (base peak).

Found: C, 62.37; H, 7.51%. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51%.

6bi: Colorless oil (decomposition at 150 °C); IR (neat) 1765, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20, 3.48 (OEt), 1.32, 4.26 (CO_2Et), 1.72, 2.06 (each 3H, s, Me), 1.76 (1H, dt, $J_{8endo,8exo}=13.0$, $J_{8endo,7}=J_{8endo,4}=3.0$, 8*endo*-H), 2.04 (1H, ddd, $J_{8exo,8endo}=13.0$, $J_{8exo,7}=8.5$, $J_{8exo,4}=3.0$ Hz, 8*exo*-H), 3.26 (1H, t, $J_{4,8endo}=J_{4,8exo}=3.0$ Hz, 4-H), 3.64 (1H, dd, $J_{7,8exo}=8.5$, $J_{7,8endo}=3.0$ Hz, 7-H); MS *m/z* 268 (M^+, 2%), 168 (base peak).

Found: C, 62.63; H, 7.43%. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.15%.

Low-Temperature Photoreaction of 1d with 2e. A solution of **1d** (3.0 g, 21.4 mmol), **2e** (13.1 ml, 107 mmol), and benzophenone (1.0 g, 5.4 mmol) in 200 ml of acetone was irradiated for 5h; the solvent was then removed. The residue was chromatographed with benzene-ethyl acetate (20 : 1) to afford 1.67 g (35%) of dimethyl 5-methoxy-3-methylphthalate (**3dez**).

Photoreaction of 1d with 2h. A solution of **1d** (3.0 g, 21.4 mmol), **2h** (7.1 ml, 107 mmol), and benzophenone (1.0 g, 5.4 mmol) in 200 ml of acetonitrile was irradiated for 2 h at room temperature; the solvent was then removed. The residue was chromatographed with benzene-ethyl acetate (2 : 1) to afford 1.28 g (31%) of **4dhn** (*endo*-CN) and 0.62 g (15%) of **4dhx** (*exo*-CN).

4dhn: Colorless needles from benzene; mp 137—139 °C; IR (KBr) 2250, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.60, 3.83 (each 3H, Me), 2.57 (1H, dd, $J_{8endo,7}=7.5$, $J_{8endo,8exo}=12.5$ Hz, 8*endo*-H), 2.83 (1H, ddd, $J_{8exo,6}=3.0$, $J_{8exo,7}=6.0$, $J_{8exo,8endo}=12.5$ Hz, 8*exo*-H), 3.29 (2H, m, 6-H, 7-H),5.42 (1H, s, 4-H); MS *m/z* 193 (M^+, 1%), 112 (base peak).

Found: C, 62.18; H, 5.74; N, 7.18%. Calcd for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25%.

4dhx: Colorless needles from benzene-ethyl acetate (2 : 1); mp 114—116 °C; IR (KBr) 2250, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.72, 3.77 (each 3H, s, Me), 2.50 (1H, ddd, $J_{8exo,6}=3.0$, $J_{8exo,7}=5.5$, $J_{8exo,8endo}=12.0$ Hz, 8*exo*-H), 2.88 (1H, dd, $J_{8endo,7}=9.0$, $J_{8endo,8exo}=12.0$ Hz, 8*endo*-H), 3.14 (1H, ddd, $J_{7,6}=3.0$, $J_{7,8}=9.0$, $J_{7,8exo}=5.5$ Hz, 7-H), 3.25 (1H, dd, $J_{6,7}=3.0$, $J_{6,8exo}=3.0$ Hz, 6-H), 5.24 (1H, s, 4-H); MS *m/z* 193 (M^+, 4%), 112 (base peak).

Found: C, 62.38; H, 5.76; N, 7.18%. Calcd for $C_{11}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25%.

Photoreaction of 1d with 2i. A solution of **1d** (3.0 g, 21.4 mmol), **2i** (10.3 ml, 107 mmol), and benzophenone (1.0 g, 5.4 mmol) in 200 ml of acetonitrile was irradiated for 5h at room temperature; the solvent was then removed. The residue was chromatographed with benzene-ethyl acetate (15 : 1) to give 0.46 g (10%) **5din** (*endo*-OEt), and 0.48 g (11%) of **5dix** (*exo*-OEt).

5din: Colorless needles from petroleum ether; mp 59—61 °C; IR (KBr) 1755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20, 3.56 (OEt), 1.78 (1H, q, $J_{8endo,1}=J_{8endo,7}=J_{8endo,8exo}=9.0$ Hz, 8*endo*-H), 2.04, 3.12 (each 3H, s, Me), 2.48 (1H, td, $J_{8exo,1}=J_{8exo,8endo}=9.0$, $J_{8exo,7}=7.0$ Hz, 8*exo*-H), 2.74 (1H, td, $J_{1,8exo}=J_{1,8endo}=9.0$, $J_{1,7}=2.0$ Hz, 1-H), 3.98 (1H, dd, $J_{7,8endo}=9.0$, $J_{7,8exo}=7.0$ Hz, 7-H), 4.92 (1H, s, 5-H); MS *m/z* 212 (M^+, 0.1%), 72 (base peak).

Found: C, 62.27; H, 7.56%. Calcd for $C_{11}H_{16}O_4$: C, 62.25; N, 7.60%.

5dix: Colorless prisms from petroleum ether; mp 45—46 °C; IR (KBr) 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.23, 3.62 (OEt), 2.00, 3.15 (each 3H, s, Me), 2.15 (2H, m, 8*endo*-H, 8*exo*-H), 3.40 (1H, dd, $J_{1,8exo}=8.0$, $J_{1,8endo}=3.0$ Hz, 1-H), 3.87 (1H, dd, $J_{7,8endo}=5.0$, $J_{7,8exo}=3.0$ Hz, 7-H), 4.83 (1H, s, 5-H); MS *m/z* 212 (M^+, 0.2%), 72 (base peak).

Found: C, 62.29; H, 7.59%. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

GC Analysis of Photoreactions between 1b or 1d and 2f, 2h, or 2i. Solutions of **1b** or **1d** (1.5 mmol), **2i** (15 mmol), and benzophenone (0.38 mmol) in 20 ml of acetonitrile were photo-irradiated at room temperature; amounts of **1b**, **1d**,

4bh, **5ci**, **5di**, and the cycloadduct **8**[8] of **2f** with dichloroethylene were then measured by the GC method, as shown in our previous report.[4] Reactions in the presence of other sensitizers were similarly analyzed; the results are given in Figs. 1 and 2.

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