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Photochemical Reactions between Dibromomaleic Anhydride and *N*-Phenylpyrrole[1]

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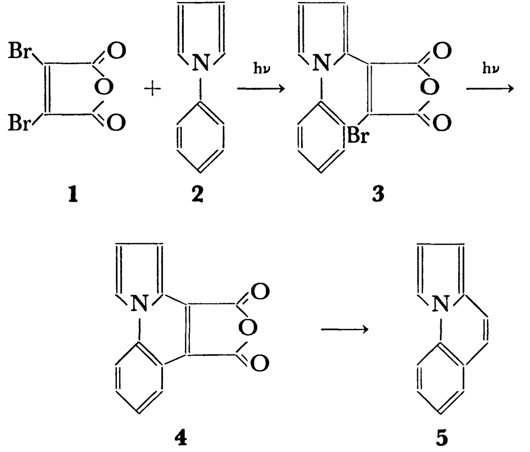
With the irradiation of dibromomaleic anhydride and *N*-phenylpyrrole, photosubstitution and photocyclization took place in succession to yield pyrrolo[1,2-a]quinoline-4,5-dicarboxylic anhydride as the final product. On the basis of energy-transfer experiments, both of the reactions were concluded to proceed *via* triplet species. Solvent effects were carefully examined and the presence of polar reaction intermediates was proposed to account for the solvent-dependent deactivation process.

The photoinduced addition between maleic anhydride and benzene is a well known example where charge-transfer complexes determine the course of photochemical reactions.[2] In the case of dibromomaleic anhydride and benzene homologues closely related to the above system, the irradiation of charge-transfer bands induced successive substitution of the two bromine atoms with phenyl groups, and further irradiation afforded phenanthrene-9,10-dicarboxylic anhydride as the final product.[3] Since the photochemical characteristic of dibromomaleic anhydride has not been reported, the mechanistic details of the reaction were investigated here by the use of *N*-phenylpyrrole, whose ionization potential is much lower than other benzene homologues.[4]

Results

Identification of the Reaction Products. After irradiation of dibromomaleic anhydride (**1**) and *N*-phenylpyrrole (**2**) with a high-pressure mercury lamp, the reaction mixture was treated with silica-gel column chromatography, and a crystalline material was obtained. On the basis of the spectroscopic data, the crystalline material was suggested to be 3-bromo-4-(*N*-phenyl-2-pyrryl)-2,5-furandione (**3**). On further irradiation, **3** was quantitatively converted to pyrrolo[1,2-a]quinoline-4,5-dicarboxylic anhydride (**4**). The structure of **4** was deduced from the spectroscopic data and was verified by the fact that 5,6-benzopyrocholine (**5**) was obtained after the thermal decarboxylation. The overall reactions are summarized as follows:



Quantum Yields. The absolute quantum yields for the formation of **3** (called photosubstitution hereafter) in benzene solution on direct excitation were determined by irradiating the sample solution with a collimated beam of monochromatic light (334 nm). The light intensity was determined by the use of a potassium ferrioxalate actinometer. Relative quantum yields in the presence of various additives were determined by the use of a modified merry-go-round irradiation apparatus. The irradiating light from a high-pressure mercury lamp was filtered through two layers of solutions around the lamp. The growth of **3** was monitored in each case by the change in optical density at the characteristic absorption band in the electronic spectra. The total conversion was never allowed to exceed 5%. The results are summarized in Table 1, where the triplet energy of each additive is also included. Biacetyl (E_T=55 kcal/mol) also was found to sensitize the reaction, although the quantum yield was not accurately determined due to the small extinction coefficient of biacetyl. No sensitization was observed with either pyrene (E_T=49 kcal/mol) or anthracene (E_T=42 kcal/mol). In the absence of additives, the quantum yields (Φ_p) depend on the concentration of **2**. A linear correlation between the inverse of the two quantities was observed, as discussed later (Fig. 1). In the case of photocyclization from **3** to **4**, the quantum yield on the direct excitation of **3** was strongly affected by the change in solvents, as shown in Table 2. The effect of additives on the photocyclization was also investigated. The reaction was sensitized in the presence of xanthone (E_T=74), benzophenone (E_T=69), phenanthrene (E_T=62), and pyrene (E_T=49 kcal/mol). Quenching of the reaction was observed, on the other hand, when acridine (E_T=

Table 1. Quantum yields of the photosubstitution (Φ_p) in the presence of various additives[a]

Additive	Triplet energy (kcal/mol)	Φ_p
None	53.5[b]	0.050
Sensitizer		
Xanthone	74[c]	0.064
Benzophenone	69[c]	0.065
Quencher		
Cyclooctatetraene[e]	<39[d]	0.042
Oxygen[f]	23[c]	0.039

a) The benzene solution containing **1** and **2** in equal amounts (5×10^{-3} M) was irradiated with 334 nm-light. b) See Ref. 5. c) See Ref. 6. d) See Ref. 7. e) 5×10^{-4} M. f) Air-saturated solution.

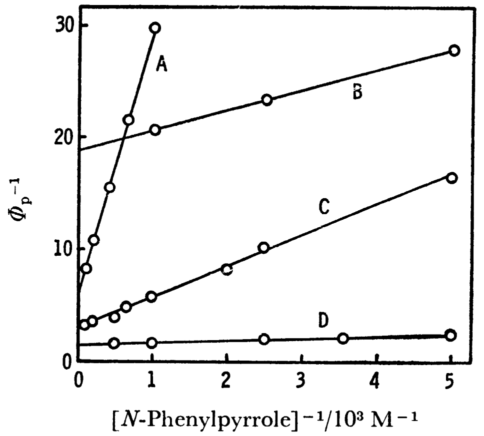


Fig. 1. Relationship between the quantum yield of **3** and the concentration of **2** in various solvents. A: Chlorobezene. B: Dichloromethane C: Diethyl ether. D: Carbon tetrachloride.

Table 2. SOLVENT EFFECTS ON THE QUANTUM YIELD OF THE PHOTOCYCLIZATION OF **3**[a] UNDER IRRADIATION WITH 436 nm-LIGHT

Solvent	Φ_p	Polarity parameter[b]
Carbon tetrachloride	0.23	32.5
Toluene	0.072	33.9
Benzene	0.070	34.5
Chlorobenzene	0.042	37.5
Diethyl ether	0.025	34.6
Dioxane	0.021	36.0
Ethylene chloride	0.009	41.9
Dichloromethane	0.007	41.1
Acetone	0.001	42.2
Acetonitrile	0.001	46.0

a) 6×10^{-5} M solutions. b) Dimroth's E_T-value. See Ref. 8.

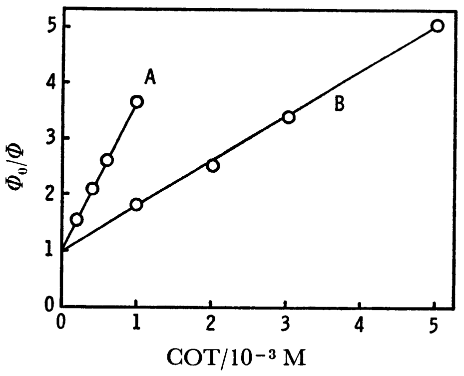


Fig. 2. Stern-Volmer plots of the reaction between **1** and **2** in dichloromethane. A: $[\mathbf{2}]=2\times10^{-4}$ M. B: $[\mathbf{2}]=1\times10^{-3}$ M.

45), anthracene ($E_T=42$), COT ($E_T<39$) and oxygen ($E_T=23$ kcal/mol) were present in the solution.

Quenching Studies. Since the photosubstitution reaction was quenched either by COT or oxygen as described above, the variation of the quantum yield was studied as a function of COT concentration. A typical example of a Stern-Volmer plot is shown in Fig. 2. The Stern-Volmer plot was invariably linear out to Φ_0/Φ values greater than 5. The quenching constant (K) was found to depend both on the concentration of **2** and also on the solvent, as summarized in Table 3. The photocyclization from **3** to **4** also gave nice Stern-Volmer plots, as shown in Fig. 3, for three different quenchers in benzene solutions. The lifetimes of the triplet state of **3** thus obtained in various solvents are summarized in Table 4.

Table 3. QUENCHING CONSTANTS (K) FOR PHOTOSUBSTITUTION REACTION UNDER IRRADIATION WITH 313 nm-LIGHT

Solvent	[**2**] (mM)	K (M^{-1})
Carbon tetrachloride	0.2	2600
	1.0	670
Diethyl ether	0.3	700
	3.0	220
Chlorobenzene	3.0	120
	10	60
Dichloromethane	0.2	2700
	1.0	620

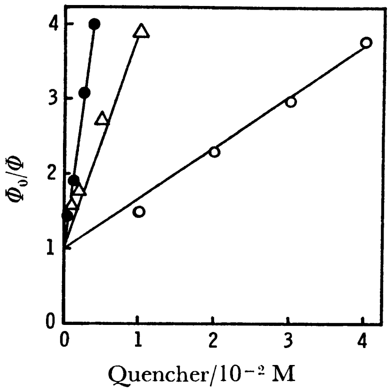


Fig. 3. Stern-Volmer plots of the photocyclization of **3** in the benzene solution (6×10^{-5} M). The reactions were quenched by the following additives (Q): COT (—●—), anthracene (—△—), and acridine (—○—).

Table 4. QUENCHING CONSTANTS (K) AND LIFETIMES (τ_0)[a] OF THE TRIPLET SPECIES IN THE PHOTOCYCLIZATION OF **3**[b] UNDER IRRADIATION WITH 436 nm LIGHT, WHEN THE REACTION WAS QUENCHED WITH COT

Solvent	K, M^{-1}	τ_0, s
Carbon tetrachloride	1.3×10^4	2.0×10^{-6}
Benzene	8.6×10^3	8.0×10^{-7}
Diethyl ether	5.2×10^3	9.0×10^{-8}
Dichloromethane	3.2×10^3	3.5×10^{-7}

a) The lifetime ($\tau_0=K/k_q$) is defined as the inverse of the sum of the rate constants for the radiationless decay and for the photocyclization of **3**. The k_q-value was estimated on the assumption that the quenching process is diffusion-controlled ($k_q=k_{\mathrm{diff}}$), where the value for k_{diff} was obtained by the use of the following equation:

$$k_{\mathrm{diff}}=\frac{8RT}{3000\,\eta}\ \mathrm{M^{-1}\,s^{-1}}\ (20\ ^\circ\mathrm{C})$$

b) 6×10^{-5} M solutions.

Discussion

Photosubstitution Reaction. On the basis of both sensitization and quenching studies, the photosubstitution reaction is clearly concluded to proceed *via* a triplet state. Results of the sensitization experiment in Table 1 suggest that the energy of the triplet state lies between 49 and 55 kcal/mol. The triplet energy of **1**, on the other hand, has been estimated to be 53.5 kcal/mol by studying the phosphorescence spectra.[5] The experimental condition for the irradiation without any additive was adjusted so that **1** alone was selectively excited. Then, it is quite reasonable to suggest that the reactive species is the triplet state of **1**. One may suggest that a charge-transfer complex between **1** and **2** would be involved in the excitation. It is true that a charge-transfer band is observed on mixing **1** and **2**, and also irradiation of the charge-transfer band induces the same reaction as above.[9] On the basis of the equilibrium constant (0.1 M^{-1}), however, it is concluded that the concentration of the charge-transfer complex is too small to make any contribution to the excitation under the present experimental conditions. When the reaction was sensitized by benzophenone, the Φ_p-value is raised by 30% (Table 1). The experimental conditions were adjusted so that neither spontaneous decay or self-quenching of excited benzophenone effectively competed with the rate of quenching induced by **1**. In other words, the excitation energy of benzophenone is expected to be transferred to **1** without any loss. Then, the difference in Φ_p-values is taken to correspond to that in the intersystem-crossing efficiency between **1** and benzophenone. On the basis of these arguments, the intersystem-crossing efficiency in **1** is estimated to be close to 0.8. Then, the following reaction scheme is suggested to explain the above experimental observations. The presence of an associated species C is assumed here in order to take into consideration the deactivation process after the reactive triplet **1** encountered **2**. Essentially the same reaction schemes have been adopted to account for the photoreaction between acenaphthylene and 1,3-pentadiene,[10] and photodimerization of 2-cyclopentenone *etc.*[11] The relevant species, **1**, **2**, **3**, sensitizer, and quencher are denoted by A, D, P, S, and Q, respectively. Under the usual steady state assumption, the quantum yield for the photosubstitution is given by Eq. (10). In the absence of Q, a linear correlation between Φ_p^{-1} and $[\mathrm{D}]^{-1}$ is expected to hold. This expectation was fulfilled, as shown in Fig. 1. The intercept and slope correspond to $(k_p+k_{-r})/(\Phi_{isc}\cdot k_p)$ and $k_{d-3}\cdot(k_p+k_{-r})/(\Phi_{isc}\cdot k_r\cdot k_p)$, respectively. Assuming the above estimated intersystem-crossing efficiency (0.8), one can evaluate a quotient, k_p/k_{-r}, as summarized in Table 5. Equations (12) and (13) indicate that the quenching constant (K) obtained from Stern-Volmer plots depends on the concentration of D. The lifetime of ^{3}A ($\tau_0=1/k_{d-3}$) and the rate constant k_r can be estimated from the K-values obtained at two different concentration of D. These results are summarized in Table 6, where k_{d-3}/k_r is also included. The values for k_{d-3}/k_r in Table 6 are in good agreement with those in Table 5. The agreement between the values obtained with two different methods may be taken to substantiate the proposed reaction scheme. The most important point in the reaction scheme is the presence of a deactivation step (Eq. (8)), which is suggested to take place after ^{3}A collides with D. The following argument affords

$$
\begin{array}{lll}
 & \text{Rate} & \\
\mathrm{A} \xrightarrow{h\nu} {}^1\mathrm{A} & \mathrm{I_a} & (1) \\
{}^1\mathrm{A} \xrightarrow{k_{d-1}} \mathrm{A} & k_{d-1}[{}^1\mathrm{A}] & (2) \\
{}^1\mathrm{A} \xrightarrow{k_{isc}} {}^3\mathrm{A} & k_{isc}[{}^1\mathrm{A}] & (3) \\
{}^3\mathrm{S} + \mathrm{A} \xrightarrow{k_e} \mathrm{S} + {}^3\mathrm{A} & k_e[{}^3\mathrm{S}][\mathrm{A}] & (4) \\
{}^3\mathrm{A} \xrightarrow{k_{d-3}} \mathrm{A} & k_{d-3}[{}^3\mathrm{A}] & (5) \\
{}^3\mathrm{A} + \mathrm{Q} \xrightarrow{k_q} \mathrm{A} + {}^3\mathrm{Q} & k_q[{}^3\mathrm{A}][\mathrm{Q}] & (6) \\
{}^3\mathrm{A} + \mathrm{D} \xrightarrow{k_r} \mathrm{C} & k_r[{}^3\mathrm{A}][\mathrm{D}] & (7) \\
\mathrm{C} \xrightarrow{k_{-r}} \mathrm{A} + \mathrm{D} & k_{-r}[\mathrm{C}] & (8) \\
\mathrm{C} \xrightarrow{k_p} \mathrm{P} & k_p[\mathrm{C}] & (9)
\end{array}
$$

$$\frac{1}{\Phi_p} = \frac{1}{\Phi_{isc}}\cdot\frac{k_p+k_{-r}}{k_p}\cdot\left(1+\frac{k_{d-3}+k_q[\mathrm{Q}]}{k_r[\mathrm{D}]}\right) \tag{10}$$

$$\Phi_{isc} = k_{isc}/(k_{isc}+k_{d-1}) \tag{11}$$

$$(\Phi_p)_0/(\Phi_p) = 1 + K[\mathrm{Q}] \tag{12}$$

$$K = k_q/(k_{d-3}+k_r[\mathrm{D}]) \tag{13}$$

$$\tau_0 = 1/K_{d-3} \tag{14}$$

Reaction scheme.

TABLE 5. KINETIC PARAMETERS FOR THE PHOTOSUBSTITUTION ESTIMATED FROM THE CONCENTRATION DEPENDENCE OF THE QUANTUM YIELDS IN VARIOUS SOLVENTS

Parameter	Solvents			
	Carbon tetrachloride	Diethyl ether	Chlorobenzene	Dichloromethane
k_{d-3}/k_r, M	8.2×10^{-5}	7.9×10^{-4}	4.6×10^{-3}	9.6×10^{-5}
k_p/k_{-r}[a]	2.9	0.57	0.31	0.07
Polarity parameter[b]	32.5	34.7	37.5	41.1

a) The intersystem crossing efficiency (0.8) was assumed in order to evaluate k_p/k_{-r} by the use of Eq. 10. b) Dimroth's E_T-value. See Ref. 8.

TABLE 6. KINETIC PARAMETERS FOR THE PHOTOSUBSTITUTION OBTAINED FROM THE DATA OF QUENCHING EXPERIMENTS IN VARIOUS SOLVENTS

Parameters	Solvents			
	Carbon tetrachloride	Diethyl ether	Chlorobenzene	Dichloromethane
k_{d-3}, s^{-1}	7.0×10^{5}	4.0×10^{7}	4.2×10^{7}	1.0×10^{6}
k_r, $(\mathrm{M\cdot s})^{-1}$	9.3×10^{9}	4.3×10^{10}	9.3×10^{9}	2.3×10^{10}
k_{d-3}/k_r, M	7.5×10^{-5}	9.3×10^{-4}	4.5×10^{-3}	4.4×10^{-5}
τ_0, s	1.4×10^{-6}	2.5×10^{-8}	2.4×10^{-8}	1.0×10^{-6}
k_{diff}, $(\mathrm{M\cdot s})^{-1}$	6.7×10^{9}	3.7×10^{10}	8.1×10^{9}	1.5×10^{10}

further evidence in favor of the presence of C. The quantum yield of **3** in dichloromethane is less than that in carbon tetrachloride by a factor of 10. It is quite unlikely that Φ_{isc} for ^{1}A is appreciably different for the two solvents. The lifetime (τ_0) of ^{3}A is also practically the same for the two cases (Table 6). Then, it is most reasonable to suggest that deactivation takes place after the collision of ^{3}A and D but before the formation of P. The associated species C is thus included in the reaction schemes. The k_r-value in Table 6 is found to be practically the same as k_{diff} in each solvent. The corresponding value in the photoreaction of the 1,3-pentadiene-acenaphthylene system has been reported to be of the order of 10^4 M^{-1} sec^{-1}.[10] The k_r-values obtained in the photodimerizations of both 2-cyclopentenone and 2-cyclohexene also are of the order of 10^8 M^{-1}sec^{-1}.[11] This comparison in k_r clearly indicates that the collision between ^{3}A and D is extraordinarily effective for producing C. It should also be noted that the quotient k_p/k_{-r} decreases with the increase in solvent polarity, as estimated by Dimroth's E_T-values (Table 5). The associated species C is expected to be a type of donor-acceptor complex, since charge-transfer absorption is observed for the system containing **1** and **2** even in their ground states. It is well known that radiationless transitions of excited DA complexes are strongly enhanced in polar solvents.[12] Then, the decrease in the quotient k_p/k_{-r} is suggested to be due to the increase in k_{-r} in the polar solvent rather than to a decrease in k_p. In this connection, it should also be noted that the lifetime (τ_0) of ^{3}A in both diethyl ether and chlorobenzene is shorter than that in either dichloromethane or carbon tetrachloride (Table 5). This is also explained as due to the contribution of donor-acceptor interactions, since the former two solvent molecules are much better electron donors than the latter. In short, it is concluded that the photosubstition reaction proceeds *via* an associated species C, which is characterized as an electron donor-acceptor complex between **1** in the triplet state and **2** in the ground state.

Photocyclization. In the presence of COT as a quencher, Stern-Volmer plots of the photocyclization reaction from **3** to **4** followed a nice straight line until more than 75% of the reaction was quenched (Fig. 3). This reaction is sensitized by the additives with $E_T>$ 49 kcal/mol, but quenched by those with $E_T<45$ kcal/mol. Thus the reactive species in this reaction is concluded to be a triplet species with energy between 45 and 49 kcal/mol. The slope of Stern-Volmer plot decreased considerably when either anthracene ($E_T=$ 42 kcal/mol) or acridine ($E_T=45$ kcal/mol) was used as a quencher. The reduction in quenching efficiency may be explained as due to the contribution of back energy-transfer from these particular quenchers to **3**. On the basis of these observation, the energy of the reactive triplet is estimated to be close to 44 kcal/mol. The quantum yield for the formation of **4** varies considerably with the change in solvents, as summarized in Table 2. Two properties of the solvents appear to be effective in reducing the quantum yield: one is the polarity as given by Dimroth's E_T-value and the other is the electron-donating ability, as can be noticed in comparing Φ_p-values between carbon tetrachloride and toluene (or benzene) solutions. A similar trend was also observed for the lifetime of **3** in various solvents (Table 4). Then, the solvent effects on these two quantities are compared in Table 7, where the values in carbon tetrachloride are taken as the reference. Fairly good correspondence is observed as far as the values for the first three solvents are concerned. The values in dichloromethane indicate, however, that the effect on the cyclization is much larger than that on the lifetime. It is rather unlikely that either the intersystem-crossing efficiency or the rate of photocyclization of **3** is so strongly reduced as to explain sufficiently the large decrease in Φ_p in polar solvents given in Table 2. A better explanation will be that the photocyclization from **3** to **4** proceeds *via* a metastable intermediate, which may revert to **3** with a strongly solvent-dependent rate constant.

TABLE 7. SOLVENT EFFECTS ON THE PHOTOCYCLIZATION OF **3**[a)]

Solvent	Relative life-time of **3**	Relative Quantum Yield of **4**
Carbon tetrachloride	1.00	1.00
Benzene	0.40	0.31
Diethyl ether	0.05	0.11
Dichloromethane	0.18	0.03

a) 6×10^{-5} M solutions.

Experimental

Materials and Equipment. Solvents and sensitizers of guaranteed grade were each purified before use. The following compounds were synthesized according to the methods given in the references in parentheses: **1** (Ref. 13, mp 115—116 °C) and **2** (Ref. 14, mp 61—62 °C). The photoproducts were isolated by the use of column chromatography on silica gel (Mallinckrot, silic acid 100 mesh). The IR, NMR, mass, and electronic spectra were recorded on a JASCO DS-301, Varian A-60, JEOL JES-01SG, and Shimadzu UV-200 spectrometer, respectively.

*Photoreaction between **1** and **2** in Preparative Scale.* A dioxane solution (100 ml) containing **1** (1.3 g) and **2** (1.4 g) was internally irradiated with a high-pressure mercury lamp (Riko-Sha UVL-700P) equipped with a pyrex water jacket in nitrogen atmosphere for 8 hr. After the solvent, **1** and **2** were almost completely removed under reduced pressure, and then the residue was subjected to column chromatography. Elution with benzene-hexane mixture afforded **3** (670 mg) and **4** (10 mg). 3-Bromo-4-(*N*-phenyl-2-pyrryl)-2,5-furandione (**3**): mp 140—141 °C; IR (KBr) 1826 and 1759 (C=O), 1248 and 1237 (COC) cm^{-1}; UV (Dioxane): λ_{max} 233 (ε 14700) and 402 nm (11400); Mass, *m/e* 319 (M$^+$) and 317; NMR (Acetone): δ 6.57 (1H, q, 4-H), 7.16 (1H, q, 5-H), 7.44 (5H, m, C_6H_5), and 7.58 (1H, q, 3-H), $J_{3,4}=2.8$, $J_{3,5}=1.8$ and $J_{4,5}=4.0$ Hz. Found: C, 53.24; H, 2.58; N, 4.40%. Calcd for $C_{12}H_8BrNO_3$: C, 52.87; H, 2.54; N, 4.40%. Pyrrolo[1,2-a]quinoline-4,5-dicarboxylic anhydride (**4**): mp 251—251.5 °C; IR (KBr): 1835 and 1769 (C=O), 1185 and 1190 (COC) cm^{-1}; UV(Dioxane): λ_{max} 241 (ε 26400), 288 (9210), 381 (4350) and 440 nm (5960); Mass, *m/e*

237 (M^+); NMR (DMSO): 6.6—8.6(m). Found: C, 70.39; H, 3.05; N, 5.74%. Calcd for $C_{12}H_7NO_3$: C, 70.89; H, 2.97; N, 5.90%.

*Decarboxylation of **4**.* Fifteen mg of **4** was dissolved into 0.5 ml of 5 M NaOH solution, and the solution was placed in a glass tube. Small amounts (0.1 g) of soda lime was added and the tube was heated above 300 °C under reduced pressure. Yellow crystal sublimed out of the tube and was identified as 5,6-benzopyrocholine (**5**)¹⁵⁾: mp 107—108 °C; UV (acetonitrile): λ_{max} 226 (ε 31000), 242 (20000), 249 (22000), 263 (9800), 275 (7900), and 348 nm (6,400).

Determination of Quantum Yields. *(A) Irradiation with a Collimated Beam*: This method was used to determine the absolute quantum yield of both the photosubstitution (at 313 and 334 nm in benzene, and at 313 nm in carbon tetrachloride) and the photocyclization reactions (at 436 nm in benzene) without any sensitizer. The light source was a Ushio 500-W super-pressure mercury arc lamp (Ushio HB-5001B). Each monochromatic light was isolated by the use of the following combined filters: (1) 313 nm: Toshiba UV-D25 glass filter, window glass (1.5 mm), and a layer (5 cm) of nickel sulfate solution (1.05 M); (2) 334 nm: Toshiba UV-D25 glass filter, a layer (5 cm) of aqueous cupric nitrate (0.05 M), and a layer (5 cm) of aqueous solution containing nickel sulfate (0.19 M) and potassium chromic sulfate (0.015 M); (3) 436 nm: A layer (5 cm) of aqueous potassium nitrate solution (2.8 M) and a layer (5 cm) of cupric sulfate(0. 035 M) in 10% aqueous ammonium hydroxide solution. The sample solution was degassed and was placed in a cylindrical cell, which was irradiated with a collimated beam of the above described monochromatic light. After the irradiation, the amounts of photoproducts (**3** or **4**) were spectrophotometrically evaluated. The intensity of the monochromatic light was determined by the use of a potassium ferrioxalate actinometer.

(B) Irradiation of Sample Tubes Assembled on a Rotating Cylinder: The relative quantum yields in the energy-transfer experiments, the concentration dependence of the quantum yields, and the solvent effects were studied by the use of the following experimental set up. Sample solutions were appropriately prepared in each experiment, and were placed in a pyrex tube (10 mm inner diameter). The required number of sample tubes were fixed on the surface of a rotating cylinder (7.5 cm diameter), which rotated at a speed of approximately 100 rpm. The center of the rotating cylinder was located 13 cm away from the center of a 400 W high-pressure mercury arc lamp (Riko-Sha UVL-400 HA). The lamp was equipped with two coaxial, Pyrex jackets, which provided two layers of filter solutions (1 cm path length for each) surrounding the light source. The following filter solutions were used in order to irradiate the samples with the lights shown below: (1) 313 nm: An aqueous solution of potassium chromate (0.0025 M) and an aqueous solution containing nickel sulfate (0.95 M) and potassium chromic sulfate (0.075 M); (2) 334 nm: An aqueous solution of cupric nitrate (0.25 M) and an aqueous solution containing nickel sulfate (0.95 M) and potassium chromic sulfate (0.075 M); (3) 436 nm: An aqueous solution of potassium nitrite (14 M). The amount of photoproducts was determined by the use of the electronic absorption spectra.

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