Photochemical Reactions between Dibromomaleic Anhydride and Benzo[*b*]thiophene[1)]

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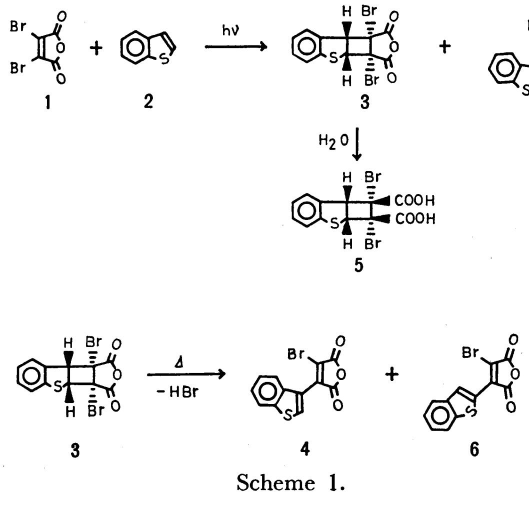
On the irradiation of dibromomaleic anhydride in the presence of benzo[*b*]thiophene, both photosubstitution and photocycloaddition are simultaneously induced. The ratio of the substituted product to the cycloadduct increased with solvent polarity, and the same Stern-Volmer plots were obtained with both of the reactions. Kinetic parameters, obtained under various concentrations of benzo[*b*]thiophene, indicate that the reactions proceed *via* a common triplet exciplex. The activation energy for the photosubstitution is higher than that for the cycloaddition by 1—2 kcal/mol, where the former reaction is considered to proceed *via* a more polar transition state than the latter.

Photochemical reaction between maleic anhydride (or maleimide) and benzene (or alkyl-substituted benzene) affords cycloaddition compounds.[2—4)] Photosubstitutions are observed, when dibromomaleic anhydride (or dibromomaleimide) is irradiated in the presence of aromatic compounds such as monosubstituted benzenes,[5)] phenylpyrrole,[6)] and indole.[7)] In the case of dibromomaleic anhydride–benzo[*b*]thiophene system, as reported in this paper, both photosubstitution and photocycloaddition proceed simultaneously. The mechanistic detail and the relationship between photosubstitution and photocycloaddition will be discussed below.

Results

Reaction Products. After irradiation of dibromomaleic anhydride (**1**) and benzo[*b*]thiophene (**2**) with a high-pressure mercury lamp, the reaction mixture was treated with silica gel column chromatography, and two crystalline materials were obtained. On the basis of the spectroscopic data, the crystalline materials were suggested to be 1-bromo-2-(3-benzo[*b*]thienyl)-maleic anhydride (**4**) and *anti*-1,2-dibromo-1,2,2a,7b-tetrahydrocyclobuta[*b*]benzo[*d*]thiophene-1,2-dicarboxylic acid (**5**). The compound **5** is a hydrolysis product of *anti*-1,2-dibromo-1,2,2a,7b-tetrahydrocyclobuta[*b*]benzo[*d*]thiophene-1,2-dicarboxylic anhydride (**3**). Thermal decomposition of **3** in acetic anhydride gave **4** (6%) and 1-bromo-2-(2-benzo[*b*]thienyl)maleic anhydride (**6**, 94%).



Scheme 1.

Quenching Studies. The variation of the quantum yields for the formation of **3** and **4** in dichloromethane solutions was studied as a function of cyclooctatetraene (COT) concentration (Fig. 1). The amounts of **3** and **4** were evaluated by the visible absorption and GLC, respectively.[8)]

The Stern-Volmer plots of both **3** and **4** gave nearly the same straight lines up to Φ_0/Φ-values near 5. The quenching constant (K)[9)] was found to depend on the concentration of **2**. Assuming that k_q equals the diffusion-controlled rate parameter, the lifetime of ^{3}**1**(τ_{obsd}) in various concentration of **2** can be estimated from the K-values. The correlation between the concentration of **2** and inverse of the τ_{obsd}-value was linear (Fig. 2). From the intercept, τ^0_{obsd} can be calculated to be 1×10^{-5} s. In addition to benzo[*b*]thiophene, kinetics were also investigated with phenylpyrrole, benzene and chlorobenzene, which gave substituted product by the photo-induced reaction with **1**.[5,6)] The results are shown in Fig. 2. Slopes of the straight lines (k_d) in Fig. 2 and the charge transfer bands of TCNE complex for each compound are summarized in Table 1.

Quantum Yields. The reactions were carried out by the use of a modified merry-go-round irradiation apparatus. The light intensity of monochromatic light (313 nm) was monitored by the use of a photochemical reaction between **1** and phenylpyrrole.[6)] The quantum yields for the formation of **4** was estimated by the ab-

Table 1. The quantum yields for the formation of the substituted products (Φ_S) and cycloaddition products (Φ_A) and k_d-values for various aromatic compounds[a)]

D-H	$h\nu_{\mathrm{CT}}$[b)] (eV)	Φ_S	Φ_A	k_d ($M^{-1}s^{-1}$)
N-Phenylpyrrole	2.28(A)[c)]	0.67	—	9.1×10^9
Benzo[*b*]-thiophene	2.35(B)[d)]	0.17	0.47	6.4×10^9
Benzene	3.23(B)[d)] 3.20(C)[e)]	0.10	—	5.2×10^8
Chlorobenzene	3.27(C)[e)]	0.08	—	7.0×10^7

a) Solvent: CCl_4. [**1**]=[D-H]=10^{-2} M. $h\nu$: 313 nm. b) $h\nu_{\mathrm{CT}}$ TCNE complex. Solvent: (A) tetrachloroethane, (B) chloroform, (c) dichloromethane. c) See Ref. 10. d) See Ref. 11. e) See Ref. 12.

Table 2. The quantum yields[a] for photocycloaddition (Φ_A) and photosubstitution (Φ_S), and the difference of activation energies in various solvents under irradiation with 313 nm-light

Solvent	Polarity parameter[b]	Φ_A	Φ_S	Φ_A/Φ_S	ΔE (kcal/mol)
Carbon tetrachloride	32.5	0.23	0.17	1.4	1.4±0.2
Diethyl ether	34.6	0.16	0.14	1.1	—
Dichloromethane	41.1	0.23	0.32	0.72	1.0±0.2
Acetonitrile	46.0	0.045	0.067	0.67	1.1±0.2

a) The values obtained by extrapolation to the infinite concentration of **2**. $[\mathbf{1}]=10^{-2}$ M. b) Dimroth's E_T-value. See Ref. 13.

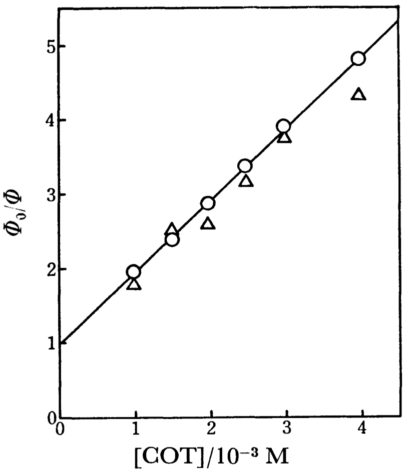


Fig. 1. Stern-Volmer Plots of photosubstitution (—○—) and photocycloaddition (—△—) in dichloromethane solution. $[\mathbf{1}]=1.5\times10^{-2}$M, $[\mathbf{2}]=1\times10^{-3}$M.

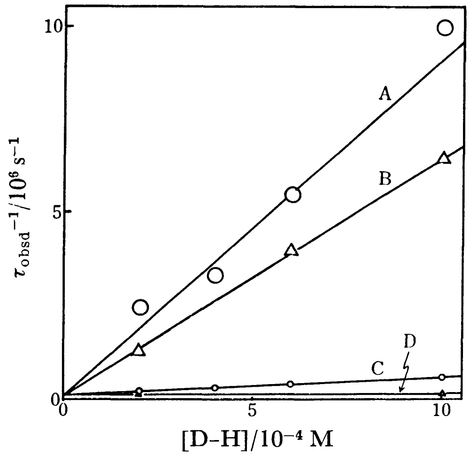


Fig. 2. Relationship between triplet lifetime and concentration of D-H in carbon tetrachloride. $[\mathbf{1}]=1\times10^{-2}$ M. A: *N*-Phenylpyrrole. B: Benzo[*b*]thiophene. C: Benzene. D: Chlorobenzene.

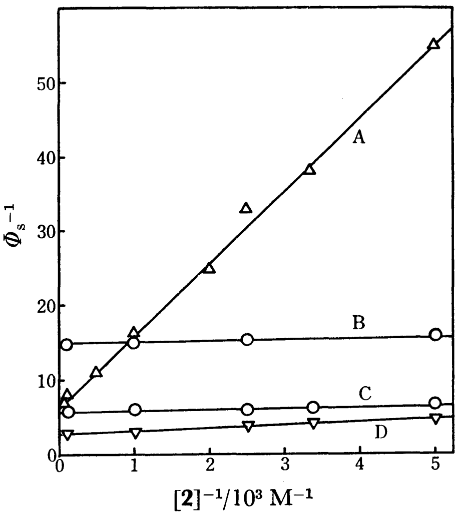


Fig. 3. Relationship between the quantum yield of **4** and the concentration of **2** in various solvents. A: Diethyl ether. B: Acetonitrile. C: Carbon tetrachloride. D: Dichloromethane.

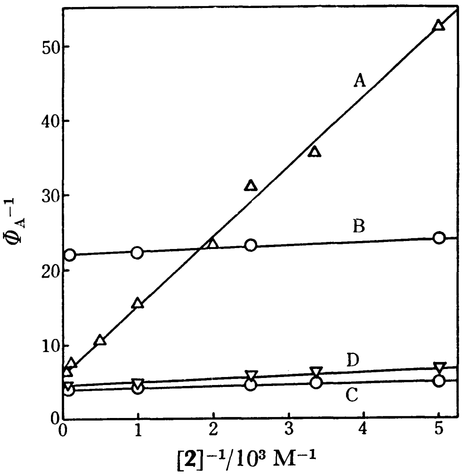


Fig. 4. Relationship between the quantum yield of **3** and the concentration of **2** in various solvents. The notations are the same as those in Fig. 3.

sorption maximum of visible spectrum. Relative yields for the formation of **3** to **4** were evaluated from the GLC peaks area of the pyrolysis products, **4** and **6**. Then the yield for the formation of **3** was calculated from that for **4** and the relative yield, **4**/**3**. The inverses of the quantum yields for the substitution and cycloaddition reactions are plotted *vs.* $[\mathbf{2}]^{-1}$ in Fig. 3 and Fig. 4, respectively. Linear relationships with different slopes and intercepts were observed with various solvents. The values for Φ_A and Φ_S at the infinite concentration of **2** are given in Table 2.

Temperature Effects. The ratio of quantum yields for formations of **4** to **3** in various solvents was measured at various temperatures. The slope of the Arrhenius

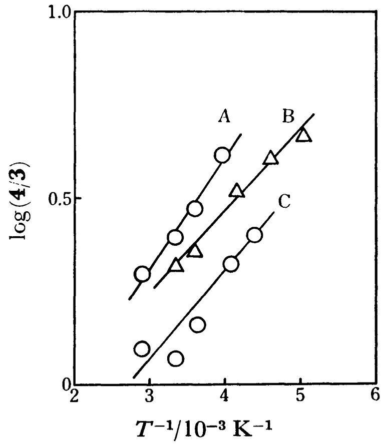


Fig. 5. Arrhenius plots of the product ratio (**4**/**3**) in various solvents. A: Carbon tetrachloride. B: Dichloromethane. C: Acetonitrile.

plots of the ratio, as shown in Fig. 5, corresponds to the difference in activation energies between photosubstitution and photocycloaddition. The difference in activation energies thus obtained also included in Table 2.

Discussion

The above experimental data clearly indicate that the cycloaddition and substitution simultaneously proceed upon the irradiation of **1** and **2**. Thermal decomposition of the cycloadduct **3** at high temperature affords substituted benzo[*b*]thiophene isomers, **4** and **6** (major product), while the formation of **6** was not noticed at all in close examination of the ^{1}H NMR spectra of the irradiated solution. In other words, the photosubstitution takes place exclusively at the 3-position of benzo[*b*]thiophene. The reactions, here investigated, may be summarized by the following scheme:

On the basis of the Stern-Volmer plots (Fig. 1), it is concluded that the triplet species is involved in the formation of both **3** and **4**. The irradiation condition for the quenching experiments is adjusted so that **1** is exculsively excited. Besides, the triplet energy of **1** (E_T=53.5 kcal/mol)[14] is located between those of **2** (E_T=68.9 kcal/mol)[15] and COT ($E_T \leq 39$ kcal/mol).[16] Therefore, the active species under discussion must be ^{3}**1**.

The triplet species is quenched by the addition of various aromatic substances as shown in Fig. 2. For a given concentration of the aromatic additive, the apparent lifetime of the triplet (τ_{obsd}) decreases with the increase in the electron-donating property of the additive. Then, the presence of donor-acceptor type interaction in the excited state is indicated. Based on the intercept of the straight lines in Fig. 2, the lifetime of the triplet in the absence of aromatic additive (τ^0_{obsd}) was estimated to be 1×10^{-5} s.

In order to account for the above experimental facts, as well as a linear correlation between $[\mathbf{2}]^{-1}$ and $\Phi_S{}^{-1}$ (or $\Phi_A{}^{-1}$) in Fig. 3 (or Fig. 4), the following reaction scheme is suggested.

Rate

$$\mathrm{A} \xrightarrow{h\nu} {}^1\mathrm{A} \qquad I_a \tag{1}$$

$${}^1\mathrm{A} \xrightarrow{k_{d-1}} \mathrm{A} \qquad k_{d-1}[{}^1\mathrm{A}] \tag{2}$$

$${}^1\mathrm{A} \xrightarrow{k_{isc}} {}^3\mathrm{A} \qquad k_{isc}[{}^1\mathrm{A}] \tag{3}$$

$${}^3\mathrm{A} \xrightarrow{k_{d-3}} \mathrm{A} \qquad k_{d-3}[{}^3\mathrm{A}] \tag{4}$$

$${}^3\mathrm{A} + \mathrm{Q} \xrightarrow{k_q} \mathrm{A} + {}^3\mathrm{Q} \qquad k_q[{}^3\mathrm{A}][\mathrm{Q}] \tag{5}$$

$${}^3\mathrm{A} + \mathrm{D} \xrightarrow{k_r} \mathrm{E} \qquad k_r[{}^3\mathrm{A}][\mathrm{D}] \tag{6}$$

$$\mathrm{E} \xrightarrow{k_{-r}} {}^3\mathrm{A} + \mathrm{D} \qquad k_{-r}[\mathrm{E}] \tag{7}$$

$$\mathrm{E} \xrightarrow{k_{d-e}} \mathrm{A} + \mathrm{D} \qquad k_{d-e}[\mathrm{E}] \tag{8}$$

$$\mathrm{E} \xrightarrow{k_A} \mathrm{P_A} \qquad k_A[\mathrm{E}] \tag{9}$$

$$\mathrm{E} \xrightarrow{k_S} \mathrm{P_S} \qquad k_S[\mathrm{E}] \tag{10}$$

$$\Phi_{\mathrm{A(or\ S)}}{}^{-1} = \frac{k_A+k_S+k_{d-e}}{\Phi_{isc}\cdot k_{\mathrm{A(or\ S)}}}\left(1+\frac{k_{d-3}+k_q[\mathrm{Q}]}{k_d[\mathrm{D}]}\right) \tag{11}$$

$$k_d = \frac{k_A+k_S+k_{d-e}}{k_A+k_S+k_{d-e}+k_{-r}}\cdot k_r \tag{12}$$

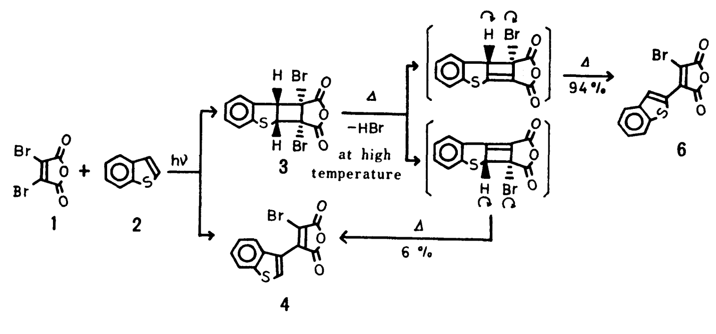
$$\frac{(\Phi_{\mathrm{A(or\ S)}})_0}{\Phi_{\mathrm{A(or\ S)}}} = 1+\frac{k_q}{k_d[\mathrm{D}]+k_{d-3}}[\mathrm{Q}] = 1+k_q\tau_{\mathrm{obsd}}[\mathrm{Q}] \tag{13}$$

$$\tau_{\mathrm{obsd}} = \frac{1}{k_d[\mathrm{D}]+k_{d-3}} \tag{14}$$

$$\tau^0_{\mathrm{obsd}} = \frac{1}{k_{d-3}} \tag{15}$$

$$\tau^{-1}_{\mathrm{obsd}} = (\tau^0_{\mathrm{obsd}})^{-1} + k_d[\mathrm{D}] \tag{16}$$

The role of donor-acceptor interaction is taken into consideration in the formation of the triplet exciplex (E) between the excited triplet and the aromatic additives. The relevant species **1**, **2** or other aromatic additives used in Fig. 2, the substituted product, the cyclo-



Scheme 2.

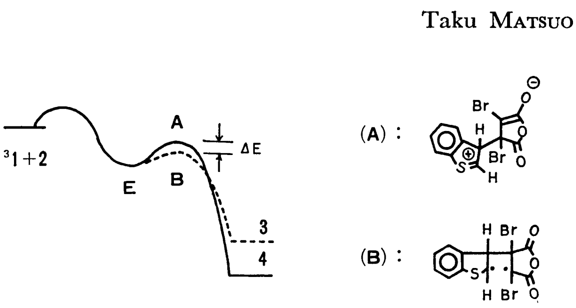


Fig. 6. Reaction diagram.

adduct, and quencher (COT) are denoted by A, D, P_S, P_A, and Q, respectively.

The linear relationships in Fig. 2 are represented by Eq. 16, while those in Figs. 3 and 4 are explained by Eq. 11. By the use of Eq. 11, the $k_d \cdot \tau^0_{obsd}$-value for dibromomaleic anhydride–benzo[*b*]thiophene system in carbon tetrachloride is evaluated to be 3.7×10^4 M^{-1} (Figs. 3 and 4). This value is in good agreement with the product between k_d (6.4×10^9 M^{-1} s^{-1}) and τ^0_{obsd} (1×10^{-5} s), which were previously obtained by the quenching experiments (Fig. 2, Table 1).

The k_d-value increases with electron-donating ability of D, as summarized in Table 1. In the case of *N*-phenylpyrrole and benzo[*b*]thiophene, the k_d-values are practically the same as k_{diff}. The large k_d-value is associated with high quantum yields ($\Phi_S + \Phi_A$). However, the variation in the k_d-value is approximately ten-times larger than that in the quantum yield. It may be that the deactivation of the triplet exciplex, as represented by Eq. 8 and k_{d-e}, becomes increasingly important as donor-acceptor interaction gets stronger.[17]

Donor-acceptor interactions are favored in polar solvents. Then, the small quantum yields of the photoproducts in acetonitrile is easily understood as due to the increased donor-acceptor interaction in the triplet exciplex in this highly polar solvent. In this connection, the quantum yields in diethyl ether are extraordinary small. Besides the polarity, donor-acceptor interaction between ^{3}A and the solvent itself should be taken into consideration, because ethers have been known to be good electron donors in the study of charge-transfer complex. The donor-acceptor interaction between ^{3}A and diethyl ether may induce quite effective deactivation of the former through radiationless transition.

The ratio of photosubstitution relative to the cycloaddition increases with the temperature and polarity of solvent (Table 2 and Fig. 5). On the basis of the above discussion, it is clear that both reactions proceed *via* the same active species (^{3}A) and the triplet exciplex (E). Since, the photosubstitution is favored in polar solvents, the electronic structure of the transition state may be closer to a polar structure (A). On the other hand, the contribution of a biradical structure (B) may be most important in the transition state of the photocycloaddition, which is at lower energy by approximately 1 kcal/mol than that of the photosubstitution as summarized in Fig. 6.

Experimental

Materials and Equipments. Dibromomaleic anhydride was prepared by the reported procedure.[18] Benzo[*b*]thiophene, COT and solvents of guaranteed grade were purified before use. The photoproducts were isolated either by sublimation or by the use of column chromatography on silica gel (Mallinckrot, silic acid 100 mesh). The IR, NMR, mass, and electronic spectra were recorded on JASCO DS-301, Varian A-60, JEOL JES-01SG, and Shimadzu UV-200 spectrometers, respectively. GLC was obtained by a Shimadzu GC-3BF gas chromatograph.

*Photoreaction between **1** and **2** in Preparative Scale.*
(A) A dioxane solution (250 ml) containing **1** (0.64 g) and **2** (0.34 g) was internally irradiated with a 400 W high-pressure mercury arc lamp (Riko-Sha UVL-400HA) equipped with pyrex jacket in a nitrogen atmosphere for 4.5 h. The pyrex jacket was filled with a filter solution (a layer (1 cm) of an aqueous solutions containing nickel sulfate (0.95 M) and potassium chromic sulfate (0.075 M)). After the solvent was completely removed under reduced pressure, **4** and **6** were isolated from the residue by sublimation (1—2 Torr, 110—150 °C). 1-Bromo-2-(3-benzo[*b*]thienyl)maleic anhydride (**4**): mp 208—209 °C; IR (KBr) 1856, 1823, and 1767 (C=O), 1244 and 1230 (COC) cm^{-1}; UV (Dioxane): λ_{max} 225 (ε 2.83×10^4), 263 (8.45×10^3), and 378 nm (1.82×10^4) ; Mass, *m/e* 310 (M^+), 308; NMR(Dioxane): δ 8,60 (1H, s, 2-H) and 7.3—8.1 (4H, m, 4-H—7-H); Found: C, 46.58; H, 1.64% Calcd for $C_{12}H_5OBrS$: C, 46.62; H, 1.63%. 1-Bromo-2-(2-benzo[*b*]thienyl)maleic anhydride (**6**): mp 146—147 °C; IR (KBr) 1846, 1816, and 1767 (C=O), 1267, 1252, and 1229 (COC) cm^{-1}; UV (Dioxane): λ_{max} 266 (ε 9.64×10^3) and 383 nm (5.7×10^3); Mass, *m/e* 310 (M^+) and 308; NMR(Dioxane): δ 8.14 (1H, s, 3-H), 7.3—8.1 (4H, m, 4-H—7-H). Found: C, 46.57; H, 1.68%. Calcd for $C_{12}H_5O_3BrS$: C, 46.62; H, 1.63%.

(B) A dichloromethane solution (3 ml) containing **1** (0.39 g) and **2** (0.21 g) was externally irradiated in a nitrogen atmosphere with a 400-W high pressure mercury arc lamp through a pyrex water jacket and window glass filter (2 mm) for 1 h. After the solvent was removed under reduced pressure, the residue was subjected to column chromatography. Elution with a hexane-benzene-ethyl acetate mixture afforded **4** (60 mg) and **5** (143 mg). *anti*-1,2-Dibromo-1,2,2a,7b-tetrahydrocyclobuta[*b*]benzo[*d*]thiophene-1,2-dicarboxylic acid (**5**)[19]: mp 151—153 °C; IR (KBr) 3452 and 3242 (OH), 1760, 1726, and 1712 (C=O) cm^{-1}; Mass, *m/e* 409 (M^+), 408 and 407; NMR (Acetonitrile): δ 4.93 (2H, q, 2-H and 3-H), 7.0—7.3 (4H, m, 4-H—7-H), $J_{2,3}=8.2$ Hz.

*Photoreaction between **1** and Chlorobenzene.* A chlorobenzene solution of **1** (1.3 g/200 ml) was internally irradiated with a 30-W low-pressure mercury arc lamp (Riko-Sha UVL 303-Q) in a nitrogen atmosphere for 15 h. The GLC analysis (column: Silicone DC 430 5% on Chamerite CS 60/80, oven temperature 210 °C) of the crude residue shows the formation of **7** (90% by peak area) accompanied with small amounts of other two products (10% by peak area). After the solvent and **1** were almost removed under reduced pressure, the residue was subjected to column chlomatography. Elution with benzene-hexane mixture afforded **7** (0.25 g). 1-Bromo-2-(*p*-chlorophenyl)maleic anhydride (**7**): mp 85—86 °C; IR (KBr) 1761 and 1839 (C=O), 1250, 1273 and 1293 (COC) cm^{-1}; Mass, *m/e* 290 (M^+), 288 and 286; NMR (CCl_4): δ 7.70(m). UV (CCl_4): λ_{max}, 339 nm ($\varepsilon = 1.40 \times 10^4$). Found: C, 41.84; H, 1.42%. Calcd for $C_{10}H_4O_3BrCl$: C, 41.78; H, 1.40%.

Quenching Experiment. The relative quantum yields (313 nm) in various quencher concentrations were measured by the use of rotating cylinder.[6] After the irradiation, the amount of photoproducts was determined by the use of either the absorption spectra or GLC analysis (column: silicon OV-17 1.5% on Diasolid L; oven temperature: 215 °C).

Temperature Effects. In the experiments above room temperatures, various solutions containing **1** (1.5×10^{-2}M) and **2**(1.5×10^{-2}M) were placed in a pyrex tube and were immersed in 1 l beaker, whose temperature was controlled by a heater within ±2 °C. In the case of temperatures below 0 °C, the sample tubes were held in a pyrex dewar vessel, filled with methanol. The temperature of dewar vessel was controlled within ±3 °C by adjusting the amount of Dry Ice. Both the dewar vessel and a 400-W high pressure mercury lamp were held in a plastic tube filled with running water. Under these conditions, sample tubes were externally irradiated through the wall of either beaker or pyrex dewar vessel for about 1 h. The amount of photoproducts was evaluated either by the GLC or by the NMR spectra.

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8) The amount of **3** was actually calculated from the peaks **4** and **6**, since the pyrolysis of **3** was completed in the GLC tubes.

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19) This compound slowly decomposed to the substituted product at room temperature.