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Photoinduced Substitution Reaction Initiated by Electron-Transfer. Photochemical Reaction of 2,3-Dichloro-1,4-naphthoquinone with Thiophenes

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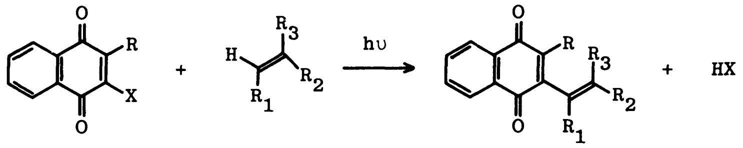
(Received November 18, 1986)

Photochemical reaction of 2,3-dichloro-1,4-naphthoquinone (**1**) with thiophenes **2** afforded 2-chloro-3-(2-thienyl)-1,4-naphthoquinones. The reaction might be initiated by the photoelectron transfer from **2** to **1**, resulting in the formation of combined products via recombination of the formed ion radicals $\mathbf{1}^{-\cdot}$ and $\mathbf{2}^{+\cdot}$ by accompanying elimination of chloro and hydro radicals. In the photoreaction, reactivity of **2** was estimated from the observed oxidation potentials of **2** and the calculated electron densities in $\mathbf{2}^{+\cdot}$.

Photoinduced reactions initiated by electron transfer are one of the recent topics. The reactions are attractive from the viewpoints of synthesis and mechanism in organic and bio-reactions.$^{1)}$ We have already reported several photosubstitution reactions induced by photoelectron transfer; photochemical reactions of 2-halo-1,4-naphthoquinones with olefins$^{2)}$ and olefin analogues$^{3)}$ (Scheme 1). In this paper, we report the photoreaction of 2,3-dichloro-1,4-naphthoquinone (**1**) with thiophenes **2** to afford 2-chloro-3-(2-thienyl)-1,4-naphthoquinones **3** which are of interest as precursors of alkylated quinones,$^{4)}$ and then discuss the reaction pathway.

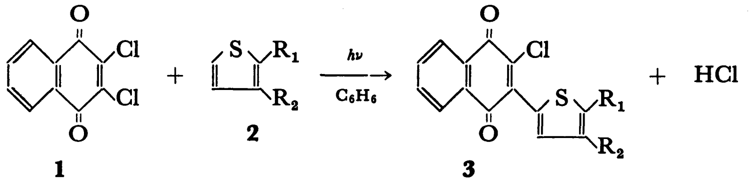


X = Cl, Br.

$R_1 = H$, $R_2,R_3 =$ Alkyl, Aryl, *O*-Alkyl, *O*-Silyl;
$R_1,R_2 = \text{-O-CH=CH-}$, $R_3 = H$;
$R_1,R_2 = \text{-NH-CH=CH-}$, $R_3 = H$.

Scheme 1. Substitution reaction of quinones with olefins initiated by photoelectron transfer.

Table 1. Photochemical Reaction of **1** with **2**



R_1	R_2		$E_{pa}{}^{a)}$/V	$I_p{}^{b)}$/eV	$v_{rel}{}^{c)}$	Yield$^{d)}$/%
I	H	(**2a**)	1.42	8.55	0.82 (**3a**)	78
Br	H	(**2b**)	1.48	8.66	1.24 (**3b**)	70
Cl	H	(**2c**)	1.50	8.70	1.51 (**3c**)	65
H	H	(**2d**)	1.54	8.80	1 (**3d**)	57
H	I	(**2e**)	1.55	—	0.11 (**3e**)	17
H	Br	(**2f**)	1.60	8.90	0.07 (**3f**)	5
H	Cl	(**2g**)	1.64	—	0.02 (**3g**)	2
CO_2H	H	(**2h**)	<1.77	—	0	0
COMe	H	(**2i**)	1.79	—	0	0
CO_2Et	H	(**2j**)	≈1.84	—	0	0
CHO	H	(**2k**)	1.85	—	0	0

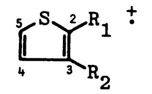
a) Anodic peak potential of **2**, error was within ±0.02 V, vs. ferrocene/ferrocenium ($[\mathbf{2}] = 10^{-3}$ mol dm^{-3}, $[n\text{-Bu}_4\text{NClO}_4] = 0.1$ mol dm^{-3}, in CH_2Cl_2, 100 mV s^{-1}, 24 °C). b) Adiabatic first ionization potential of **2**, data of Ref. 8. c) v_{rel} was the value of the initial rate in the formation of **3** relative to that in the formation of **3d** ($[\mathbf{1}] = 10^{-4}$ mol dm^{-3}, $[\mathbf{2}] = 10^{-3}$ mol dm^{-3}, in benzene, upon irradiation with light of 313 nm). d) All yields were based on consumed **1**, see Experimental part.

Results and Discussion

Photochemical reaction of quinone **1** with thiophenes **2** generally gave thienylquinones **3** (Table 1). Thiophenes **2a—g** successfully afforded **3a—g**, but the photoreaction of **2h—k** resulted in vain.[5] To explain reactivities of **2**, we tried to measure the oxidation potentials $E_{1/2}$ of **2**. All the thiophenes (**2**) were electrooxidized irreversibly,[6] and their anodic peak potentials E_{pa} are listed in Table 1. The order of their E_{pa} is supposed to be equal to that of their $E_{1/2}$ because the E_{pa} is nearly linear with the ionization potential I_P; $E_{pa}=0.501\ I_P-2.68$ (correlation coefficient $=99.8\%$).[7] As shown in Table 1, thiophenes **2a—g** whose E_{pa} were smaller than 1.7 V reacted with **1** to give **3a—g**, and **2h—k** whose E_{pa} were greater than 1.7 V did not react. In the cases of 3-halothiophenes **2e—g**, the increase in their E_{pa} suppressed their reactivities v_{rel}, the value of the initial rate in the formation of **3** relative to that in the formation of **3d**. When **2d** was added to a benzene solution of **1**, a new absorption band ($\lambda_{max}=422$ nm, the formation constant $K=0.08\ dm^3\ mol^{-1}$ at 22 °C[9]) appeared. In the ground state, thiophene **2d** formed apparently the charge-transfer (CT) complex with **1** absorbing light of wavelengths above 500 nm. Selective irradiation of the CT band (514.5 nm-irradiation, see Experimental part) led to the formation of **3d**. In the initial stage of the reaction, therefore, photoelectron transfer could occur from **2a—g** to **1**.

In order to understand the high regioselectivity in the reactions affording **3a—g** as well as less reactivity of 3-halothiophenes **2e—g**, we calculated the electron densities q in the cation radials of **2** ($\mathbf{2}^{\overset{+}{\cdot}}$) formed by the photoelectron transfer process by using Hückel molecular orbital (HMO) method (Table 2). In the cases of **2a—d**, the substitution reaction occurred at the lowest q position. This position is the electron-poorest in $\mathbf{2}^{\overset{+}{\cdot}}$, which must be attacked by the anion radical of **1** ($\mathbf{1}^{\overset{-}{\cdot}}$) more easily than any other position. On the other hand, in the cases of 3-substituted thiophenes **2e—g**, the lowest q position is crowded with iodo, bromo, and chloro atoms on its neighbouring carbon atom. Such a situation could make attacking by the fairly bulky $\mathbf{1}^{\overset{-}{\cdot}}$ difficult, so the substitution occurred at the second lowest q position sterically less hindered. The q values of C-5 atom in the cation radicals of 3-halothiophenes **2e—g** are over

Table 2. Calculated Electron Density q of $\mathbf{2}^{\overset{+}{\cdot}}$ [a)]



$\mathbf{2}^{\overset{+}{\cdot}}$

R_1	R_2		C-2	C-3	C-4	C-5
I	H	($\mathbf{2a}^{\overset{+}{\cdot}}$)	(0.764)	0.877	1.012	0.646
Br	H	($\mathbf{2b}^{\overset{+}{\cdot}}$)	(0.764)	0.874	1.014	0.641
Cl	H	($\mathbf{2c}^{\overset{+}{\cdot}}$)	(0.742)	0.884	1.003	0.637
H	H	($\mathbf{2d}^{\overset{+}{\cdot}}$)	0.623	0.932	0.932	0.623
H	I	($\mathbf{2e}^{\overset{+}{\cdot}}$)	0.586	(0.955)	0.983	0.712
H	Br	($\mathbf{2f}^{\overset{+}{\cdot}}$)	0.583	(0.950)	0.991	0.711
H	Cl	($\mathbf{2g}^{\overset{+}{\cdot}}$)	0.586	(0.950)	0.978	0.698

a) HMO calculation (ω-technique), see Ref. 10. Parenthesis indicates the position which possesses no hydrogen.

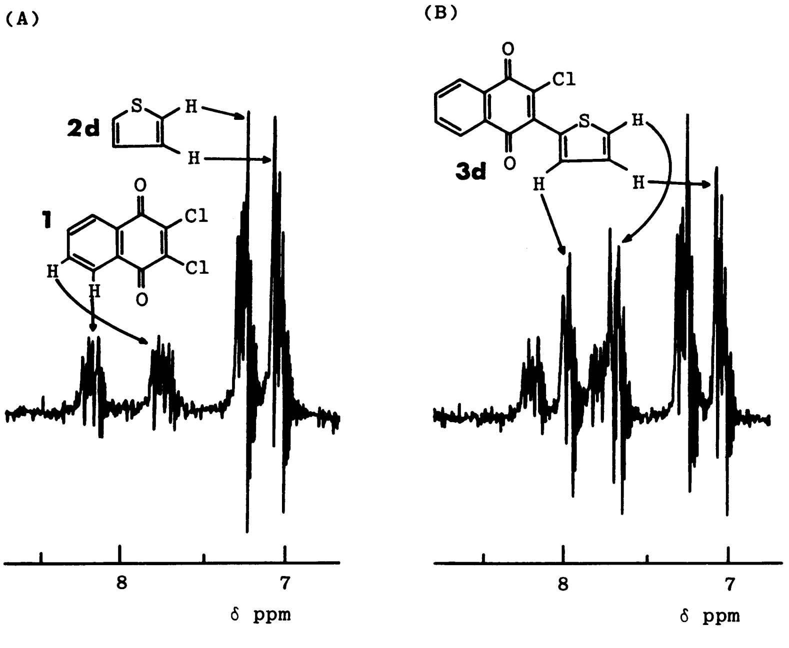
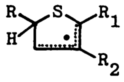


Fig. 1. ¹H NMR spectra observed in a CCl_4 solution of **1** and **2d**. (A) In the dark, (B) during irradiation.

0.69 and greater than those of highly reactive thiophenes **2a**—**d**. So the relatively high *q* values of C-5 atom in **2e**$^{\cdot+}$, **2f**$^{\cdot+}$, and **2g**$^{\cdot+}$ might suppress their reactivities. Thus, the experimental results could be clearly explained by simple HMO calculation.



4·

As shown in Fig. 1, in all the cases in which **3** were obtained except for **3a** and **3g**, photo-^{1}H CIDNP signals were observed at the protons in the thienyl moiety of **3**. The polarized patterns indicated that at least the structure of **4·** might exist in the course of the reaction and that all the radical pairs were in the triplet multiplicity.11)

Under the conditions (see footnote a) in Table 1), the CT state in the ground state was much less than 1% (about 0.08% in **2d**) and the absorption at 313 nm was mainly due to quinone **1**. Upon irradiation with light of 313 nm, the local excitation of **1** was dominant and the CT excitation was negligible. Considering the fact that **1** photoreacted with various olefins via the triplet quenching mechanism,12) the initially formed singlet excited state of **1** might immediately intersystem-cross to the triplet excited state, where it was quenched by **2** in the ground state to give the ion radical pair $^3(\mathbf{1}^{\cdot-}\cdots\mathbf{2}^{\cdot+})$. Above results lead us to the reaction mechanism in Scheme 2.

Experimental

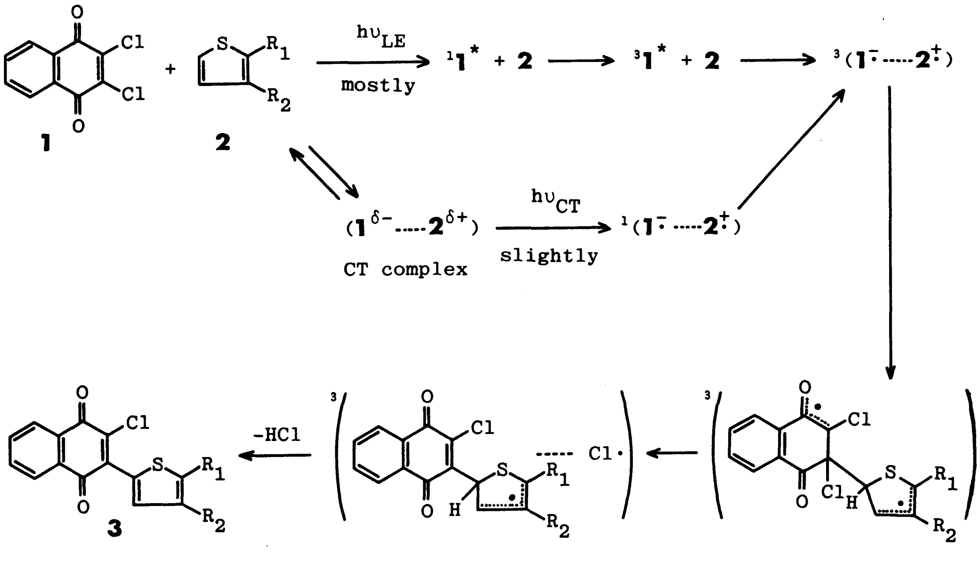
Apparatus. All melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. Ultraviolet and visible spectra were measured with a Shimadzu UV-200 spectrometer. Infrared spectra were measured with a JASCO IRA-1 spectrometer. Normal ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX400 instrument; chemical shifts (δ) are expressed in parts per million relative to tetramethylsilane. Mass spectra were measured with a JEOL JMS-DX-300 spectrometer. HPLC analyses were carried out with a Waters liquid chromatograph equipped with a LiChrosorb RP-18 column. The elemental analyses were performed at the Microanalysis Center of Kyoto University.

Materials. Reagent-grade solvents were simply distilled and used except otherwise noted. Quinone **1**, thiophenes **2b**—**d**, **2f**, and **2h**—**k** were commercially available and used after distillation. Thiohenes **2a**,13) **2e**,14) and **2g**15) were synthesized according to the procedure in the literature.

Preparation of 2-Chloro-3-(2-thienyl)-1,4-naphthoquinones 3. General Procedure: A benzene solution (700 ml) of **1** (0.7 mmol) and 10 equiv of **2** (7 mmol) was irradiated with a high-pressure mercury arc lamp (300 W) through an aqueous $CuSO_4$ solution filter under argon atmosphere at room temperature. After irradiation for a suitable time (1 h for **3a**—**d** and **3g**, 3 h for **3e**, and 12 h for **3f**), the starting quinone **1**, thiophene **2**, and the photosubstituted product **3** were isolated by using flash column chromatography on silica gel with hexane and ether as eluents. Recrystallization from dichloromethane and hexane gave a pure sample. All yields were based on consumed **1**.

2-Chloro-3-(5-iodo-2-thienyl)-1,4-naphthoquinone (3a): 78% yield; red needles; mp 151.5—152 °C; UV ($CHCl_3$) 466 nm (ε 5450); IR (KBr) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.37 (1H, d, *J*=4 Hz, 4-H), 7.74 (1H, d, *J*=4 Hz, 3-H), 7.77—7.81 (2H, m), and 8.16—8.20 (2H, m); MS (70 eV) *m/z* (rel intensity) 400, 402 (M$^+$; 100, 34), 365 (M$^+$ −Cl; 45), 337 (M$^+$ −Cl—CO; 21), 273 and 275 (M$^+$ −I; 37, 18); Found: C, 41.76; H, 1.48; Cl, 8.87; I, 31.76%; M$^+$, 399.8822 and 401.8796. Calcd for $C_{14}H_6ClIO_2S$: C, 41.97; H, 1.51; Cl, 8.85; I, 31.68%; M, 399.8824 and 401.8794.

2-(5-Bromo-2-thienyl)-3-chloro-1,4-naphthoquinone (3b): 70% yield; red plates; mp 153—153.5 °C; UV ($CHCl_3$) 460 nm



Scheme 2. Proposed mechanism for photoreaction of **1** with **2** on 313 nm-irradiation. *hν*$_{LE}$: The local excitation of **1**, *hν*$_{CT}$: The excitation of the CT complex.

(ε 4500); IR (KBr) 1665 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.17 (1H, d, J=4 Hz, 4-H), 7.75—7.80 (2H, m), 7.86 (1H, d, J=4 Hz, 3-H), and 8.12—8.20 (2H, m); MS (70 eV) m/z (rel intensity) 352, 354, 356 (M^+; 75, 100, 31), 317, 319 (M^+ −Cl; 47, 50), 289, 291 (M^+ −Cl—CO; 22, 22), 273, and 275 (M^+ −Br; 71, 29); Found: C, 47.51; H, 1.64; Br, 22.46; Cl, 9.97; S, 9.23%; M^+, 351.8960, 353.8936, and 355.8914. Calcd for $C_{14}H_6BrClO_2S$: C, 47.55; H, 1.71; Br, 22.60; Cl, 10.03; S, 9.07%; M, 351.8961, 353.8931, 353.8941, and 355.8912.

2-Chloro-3-(5-chloro-2-thienyl)-1,4-naphthoquinone (3c): 65% yield; red needles; mp 141—141.5 °C; UV ($CHCl_3$) 426 (sh, ε 4500), 445 (sh, 5000), and 463 nm (5100); IR (KBr) 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.05 (1H, d, J=4 Hz, 4-H), 7.77—7.82 (2H, m), 7.94 (1H, d, J=4 Hz, 3-H), and 8.16—8.20 (2H, m); MS (70 eV) m/z (rel intensity) 308, 310, 312 (M^+; 76, 61, 12), 273, 275 (M^+ −Cl; 100, 36), 245, and 247 (M^+ −Cl—CO; 36, 12); Found: C, 54.15; H, 1.79; Cl, 22.95; S, 10.46%; M^+, 307.9465, 309.9433, and 311.9403. Calcd for $C_{14}H_6Cl_2O_2S$: C, 54.39; H, 1.96; Cl, 22.93; S, 10.37%; M, 307.9466, 309.9436, and 311.9406.

2-Chloro-3-(2-thienyl)-1,4-naphthoquinone (3d): 57% yield; red prisms; mp 95 °C; UV ($CHCl_3$) 275 (ε 23000), 320 (50000), and 441 nm (4400); IR (KBr) 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.22 (1H, dd, J=4 and 5 Hz, 4-H), 7.73 (1H, dd, J=1 and 5 Hz, 5-H), 7.75—7.79 (2H, m), 7.95 (1H, dd, J=1 and 4 Hz, 3-H), and 8.13—8.18 (2H, m); ^{13}C NMR ($CDCl_3$) δ=181.86 (s), 177.62 (s), 139.68 (s), 138.10 (s), 134.11 (d, C-3), 134.07 (d), 134.02 (d), 132.28 (d, C-5), 131.44 (s), 131.12 (s), 130.91 (s), 127.30 (d), 126.87 (d), and 126.57 (d, C-4); MS (70 eV) m/z (rel intensity) 276, 274 (M^+; 87, 37), 239 (M^+ −Cl; 100), and 211 (M^+ −Cl—CO; 30); Found: C, 60.96; H, 2.43; Cl, 12.78; S, 11.64%; M^+, 273.9856 and 275.9826. Calcd for $C_{14}H_7ClO_2S$: C, 61.21; H, 2.57; Cl, 12.90; S, 11.67%; M, 273.9855 and 275.9826.

2-Chloro-3-(4-iodo-2-thienyl)-1,4-naphthoquinone (3e): 17% yield; red needles; mp 141—143 °C; UV ($CHCl_3$) 444 nm (ε 4060); IR (KBr) 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.77 (1H, d, J=1 Hz, 5-H), 7.78—7.82 (2H, m), 7.92 (1H, d, J=1 Hz, 3-H), and 8.16—8.22 (2H, m); MS (70 eV) m/z (rel intensity) 400, 402 (M^+; 100, 30), 365 (M^+ −Cl; 58), 337 (M^+ −Cl—CO; 25), 273, and 275 (M^+ −I; 12, 5); Found: m/z 399.8823 and 401.8791. Calcd for $C_{14}H_6ClIO_2S$: M, 399.8824 and 401.8794.

2-(4-Bromo-2-thienyl)-3-chloro-1,4-naphthoquinone (3f): 5% yield; orange needles; mp 125—127 °C; UV ($CHCl_3$) 433 nm (ε 3960); IR (KBr) 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.61 (1H, d, J=1 Hz, 5-H), 7.78—7.82 (2H, m), 7.88 (1H, d, J=1 Hz, 3-H), and 8.16—8.21 (2H, m); MS (70 eV) m/z (rel intensity) 352, 354, 356 (M^+; 73, 100, 30), 317, 319 (M^+ −Cl; 69, 70), 289, 291 (M^+ −Cl—CO; 26, 27), 273, and 275 (M^+−Br; 12, 5); Found: m/z 351.8961, 353.8934, and 355.8916. Calcd for $C_{14}H_6BrClO_2S$: M, 351.8961, 353.8931, 353.8941, and 355.8912.

2-Chloro-3-(4-chloro-2-thienyl)-1,4-naphthoquinone (3g): 2% yield; red needles; mp 143—144 °C; UV ($CHCl_3$) 434 nm (ε 5730); IR (KBr) 1670 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.51 (1H, d, J=1.5 Hz, 5-H), 7.78—7.83 (2H, m), 7.84 (1H, d, J=1.5 Hz, 3-H), and 8.17—8.21 (2H, m); MS (70 eV) m/z (rel intensity) 308, 310, 312 (M^+; 75, 58, 11), 273, 275 (M^+ −Cl; 100, 35), 245, and 247 (M^+ −Cl—CO; 45, 16); Found: m/z 307.9465, 309.9438, and 311.9412. Calcd for $C_{14}H_6Cl_2O_2S$: M, 307.9466, 309.9436, and 311.9406.

Measurement of v_{rel}. A benzene solution (1 ml) of **1** (0.1 μmol) and **2** (1 μmol) was irradiated with light of 313 nm and sampled at an appropriate interval. The molar quantity of **3** was determined by measuring the area of HPL chromatogram (H_2O-MeOH=1/9) and plotted versus time. The initial rate in the formation of **3** was determined from a slope of the straight line. The value of v_{rel} was obtained by dividing each rate by the rate in the formation of **3d**.

Measurement of E_{pa} of Thiophenes 2. Electrochemical measurement was performed with PAR Model 174 polarographic analyzer, a standard H-cell, glassy carbon (working electrode), and a platinum wire (counter electrode). The solution was 10^{-3} mol dm^{-3} in **2**, in a 0.1 mol dm^{-3} tetrabutylammonium perchlorate-dried dichloromethane solution. All the cyclic voltammograms were recorded at 24 °C under single sweep conditions (scan rate; 100 mV s^{-1}). Anodic peak potentials were corrected vs. ferrocene/ ferrocenium. The peak potentials were measured with an error of ±0.02 V. It was necessary to repeat polishing of the electrode during the experiment, because thiophene polymers and others⁶⁾ were frequently adsorbed on the electrode surface.

Examination of CT Excitation. When thiophene **2d** was added to a benzene solution of quinone **1**, color of the solution was turned from pale yellow to pale orange, owing to the formation of the CT complex of **1** with **2d**. In a benzene solution, **1** had no absorption at wavelengths above 500 nm, but the CT complexes had the absorption in the region. For selective irradiation of the CT complex, NEC GLS 3300 Argon ion laser (514.5 nm, 1 W) was used. After irradiating a benzene solution of **1** and **2d** for a few minutes, **3d** was detected by thin-layer chromatography.

Observation of ^{1}H CIDNP Signals. Suitable amounts of **1** and **2** were dissolved in CCl_4, $CDCl_3$, or C_6D_6. The sample was irradiated in a Pyrex glass NMR sample tube with a high-pressure mercury arc projector lamp at room temperature and the ^{1}H NMR signals were recorded before, during, and after irradiation by a JEOL JNM-PS-100 instrument.

We thank Dr. Atsushi Terahara and Mr. Kohji Ichimori, Dr. Satoshi Okazaki and Mr. Kouichi Nozaki, and Mr. Ken Hosoya, Kyoto University, for their help on calculation, measurement of E_{pa}, and HPLC analyses.

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