Photoinduced Electron Transfer Reaction of Pyrazoline Derivatives. Formation of Rearrangement Product

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The initial process of photoinduced electron transfer (PET) between electron deficient sensitizers and *r*-3-(methoxycarbonyl)-*t*-4-(*para*-substituted-phenyl)-3,5,5-trimethyl-1-pyrazolines **1** was investigated. Fluorescence quenching rate constants of the sensitizers by **1** and PET decomposition quantum yields of **1** reflect that the stability of the generated radical cations of **1** and the back-electron transfer play important roles in the reactivity. The generated radical cations of **1** followed by nitrogen elimination gave cyclopropane derivatives **2** and/or aryl migrated olefins **3**. Product distributions between the cyclopropanes **2** and the olefins **3** depend on the *para*-substituent of the phenyl ring of **1**. Semiempirical MO calculations (AM1) of the radical cations of **1** suggest the location of the spin and the charge governing the product distribution.

After the report of the reaction of a singlet excited azoalkane with CCl_4,[1] the photoinduced electron transfer (PET) reaction of azoalkanes has been investigated and the behavior of the radical cation of azoalkanes is gradually being clarified.[2-5] However, the study of the initial step in the reaction, an electron transfer process, is not well understood. Previously, we reported that *r*-3-(methoxycarbonyl)-*t*-4-phenyl-3,5,5-trimethyl-1-pyrazoline, **1c**, was decomposed by 9,10-dicyanoanthracene (DCA) sensitization and yielded a phenyl-migrated olefin, **3**, which was not obtained by direct photolysis and thermolysis. This reaction proceeded through an electron transfer from a pyrazoline molecule to a singlet excited sensitizer, and the olefin, **3c**, was produced from the radical cation of **1c**.[3] We next synthesized the derivatives of **1c**, the *para*-positions of the phenyl ring being substituted by a methoxy, methyl, and cyano group, **1a**, **1b**, and **1d**, respectively (Figure 1).

In this paper, we report that the stability of the generated radical cation plays an important role in the reactivity and the product distribution. Initially, we examined the fluorescence quenching rate constants of the sensitizers by the pyrazolines, **1**, and their PET decomposition quantum yields. During the next stage, the product analyses of the PET reaction of **1** were carried out. In addition to the cyclopropane formation, the olefin production implies the presence of a radical cation intermediate and the aryl migration process among the PET reactions of **1**. The product distributions depend on both the sensitizers employed and the *para*-substituents of the aryl ring of the pyrazolines, **1**. Furthermore, to obtain insight into quantitative information about the electronic properties of both the ground state neutrals **1** and the radical cations $\mathbf{1}^{\cdot+}$, semiempirical molecular orbital calculations were carried out using the AM1 method.[6] From these examinations, we clarified the initial process of the electron transfer reaction between the singlet excited sensitizer and the pyrazoline derivative.

Experimental Section

Materials. The sensitizers were purified by recrystallization. Spectrophotomeric grade (Dotite Co.) acetonitrile and dichloromethane were used in photochemical studies. The pyrazolines were synthesized as described below. The values in parentheses are isolated yields, and significant amounts of the starting materials were recovered in each case.

***r*-3-(Methoxycarbonyl)-*t*-4-phenyl-3,5,5-trimethyl-1-pyrazoline (1c).** Four g (23 mmol) of methyl α-methylcinnamate was added dropwise to a reddish THF solution of 2-diazopropane which was synthesized from 20.0 g (0.28 mol) of acetone hydrazone and 182 g of activated manganese dioxide (Kodak) in THF solution.[7] The solution was stirred for 6 h until the reddish color disappeared. After removal of the solvent by rotary evaporation, the product was purified by flash column chromatography (silica gel, benzene) and recrystallized from *n*-hexane. **1c** was obtained as colorless crystals: mp 38–39 °C (0.89 g, 16% yield); UV (acetonitrile) λ_{max} (ϵ) 333 nm (108 M^{-1} cm^{-1}); ^1H NMR (270 MHz, $CDCl_3$) δ = 6.80–7.50 (5H, m), 3.80 (3H, s), 3.34 (1H, s), 1.53 (3H, s), 1.40 (3H, s), 1.32 (3H, s). Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.26; H, 7.49; N, 11.46.

The stereochemistry of **1c** was determined by X-ray diffraction[8] and ^1H NMR (270 MHz, $CDCl_3$) containing a shift reagent (0.33 weight ratio of Eu-DPM to **1c**). Signals at δ = 3.80, 3.34, 1.53, 1.40, and 1.32 were shifted to 4.26, 3.68, 2.16, 1.63, and 1.54, respectively.

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(8) Colorless crystals of **1c** are orthorhombic, the space group is $P2_12_12_1$ with a = 110.082(2) Å, b =16.656(2) Å, c = 8.069(3) Å, V = 1355.1(6) Å^3, Z = 4, and D_c = 1.2242 g cm^{-3}. The final R value was 0.0499 for 1157 reflections with $1 > 2\ \sigma(i)$.

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***r*-3-(Methoxycarbonyl)-*t*-4-(*p*-methoxyphenyl)-3,5,5-trimethyl-1-pyrazoline (1a).** **1a** was prepared by the same method as **1c** from methyl α-methyl-*p*-methoxycinnamate (1.5 g, 7.0 mmol) and purified by flash column chromatography (silica gel, benzene) followed by recrystallization from ethanol: mp 61–62 °C (0.65 g, 34% yield); UV (acetonitrile) λ_{max} (ϵ) 334 nm (130 M^{-1} cm^{-1}). ^1H NMR (60 MHz, $CDCl_3$) δ=6.75–7.10 (4H, m), 3.80 (6H, s), 3.30 (1H, s), 1.52 (3H, s), 1.40 (3H, s), 1.31 (3H, s). Anal. Calcd for $C_{15}H_{20}N_2O_3$: C, 65.19; H, 7.30; N, 10.14. Found: C, 65.48; H, 7.41; N, 10.45. Similarity of ^1H NMR spectra of **1a** and **1c** revealed that both pyrazolines have the same stereochemistry.

***r*-3-(Methoxycarbonyl)-*t*-4-(*p*-methylphenyl)-3,5,5-trimethyl-1-pyrazoline (1b).** **1b** was prepared by the same method as **1c** from methyl α-methyl-*p*-methylcinnamate (1.6 g, 8.4 mmol) and purified by flash chromatography (silica gel, benzene) followed by distillation to give a clear oil: bp 45 °C/3 mmHg (0.09 g, 4% yield); UV (acetonitrile) λ_{max} (ϵ) 333 nm (132 M^{-1} cm^{-1}); ^1H NMR (60 MHz, $CDCl_3$) δ = 7.15 (2H, d, J = 8 Hz), 6.92 (2H, d, J = 8 Hz), 3.79 (3H, s), 3.31 (1H, s), 2.34 (3H, s), 1.54 (3H, s), 1.40 (3H, s), 1.32 (3H, s); HRMS Calcd for $C_{15}H_{20}N_2O_2$ 260.1524, found 260.1531. Similarity of ^1H NMR spectra of **1b** and **1c** reveals that both pyrazolines have the same stereochemistry.

***r*-3-(Methoxycarbonyl)-*t*-4-(*p*-cyanophenyl)-3,5,5-trimethyl-1-pyrazoline (1d).** **1d** was prepared by the same method as **1c** from methyl α-methyl-*p*-cyanocinnamate (0.85 g, 4.2 mmol) and purified by flash chromatography (silica gel, benzene) followed by recrystallization from methanol; mp 84–85 °C (0.13 g, 11% yield); UV (acetonitrile) λ_{max} (ϵ) 332 nm (136 M^{-1} cm^{-1}); ^1H NMR (60 MHz, $CDCl_3$) δ = 7.62 (2H, d, J = 8 Hz), 7.17 (2H, d, J = 8 Hz), 3.82 (3H, s), 3.43 (1H, s), 1.53 (3H, s), 1.42 (3H, s), 1.32 (3H, s). Anal. Calcd for $C_{15}H_{17}N_3O_2$: C, 66.40; H, 6.32; N, 15.49. Found: C, 66.59; H, 6.34; N, 15.73. Similarity of ^1H NMR spectra of **1d** and **1c** reveals that both pyrazolines have the same stereochemistry.

Fluorescence Quenching Studies. The quenching rate constants (k_q) of the fluorescence of the sensitizers (DCA, 1,4-dicyanonaphthalene, DCN, and 2,4,6-triphenylpyrylium tetrafluoroborate, TPT) by the pyrazolines were determined by a Stern–Volmer-type plot of the fluorescence intensity versus the concentration of **1**'s. The fluorescence was measured in acetonitrile in the presence of the pyrazoline derivatives under an argon atmosphere. Fluorescence lifetimes of DCA and DCN measured by the single photon counting method (Horiba NAES-1100) and that of TPT reported in the literature[9] were used to determine the quenching rate.

Oxidation Potentials of the Pyrazolines. Oxidation potentials of **1a-d** and 3-(methoxycarbonyl)-3,5,5-trimethyl-1-pyrazoline, (**4**) (10 mM) were measured by cyclic voltammetry (BAS CV-1B) at a platinum electrode in argon-saturated dry acetonitrile with 0.10 M tetraethylammonium perchlorate as the supporting electrolyte. The scan speed was 200 mV s^{-1}, and the reference electrode was the SCE. Obtained peaks were irreversible in all cases, and the oxidation potentials were determined from the half-peak potentials.

Decomposition Quantum Yield (Φ_{obs}). The decomposition quantum yield of **1c** (10 mM) by DCA (0.23 mM) sensitization was measured by the irradiation of 405 nm light from a 400-W high pressure mercury arc lamp, HPML, through a Toshiba L39 glass filter. Light intensity was determined by potassium tris(oxalato)ferrate (III) actinometry,[10] and the conversion (<5%) of **1c** was determined by HPLC.

Relative Rate of Decomposition (k_{rel}). Solutions of pyrazolines (10 mM) in the presence of DCA (0.23 mM) in acetonitrile were degassed by five freeze–pump–thaw cycles and were irradiated by 405 nm light from a 1-kW HPML through a $CuSO_4$ + $NaNO_2$ + NH_4OH solution filter[11] in a merry-go-round apparatus. Conversions of the pyrazolines were determined by HPLC to evaluate the values of k_{rel}.

Reactions. Thermolysis. Ten mg of the pyrazoline **1c** was sealed in a tube under vacuum and thermolyzed at 140 °C for 3.5 h. Product yield was determined by GC.

Direct Photolysis. Degassed acetonitrile solution of **1c** (10 mM) was irradiated at 366 nm for 3.5 h by a 1-kW HPML with a Toshiba UVD36B glass filter to isolate the 366 nm light. After the decomposition monitored by HPLC was complete, product yield was determined by GC.

Triplet-Sensitized Photolysis. In the presence of 28 mM benzophenone, 10 mM **1c** in acetonitrile was irradiated by 366 nm light from a 1-kW HPML with a Toshiba UVD36B glass filter. After the decomposition monitored by HPLC was complete, product yield was determined by GC.

PET Photolyses. Acetonitrile solutions of 10 mM of the pyrazolines and 0.23 mM of DCA or 3.0 mM of TPT were irradiated at 405 nm by a 1-KW HPML with a Toshiba L39 glass filter, and the solutions of 5.0 mM pyrazolines (ϵ_{313} of **1a**, **1b**, **1c**, and **1d** are 22, 40, 21, and 41 M^{-1} cm^{-1}, respectively) and 1.4 mM DCN (ϵ_{313} is 8,200 M^{-1} cm^{-1}) were irradiated at 313 nm by a 400-W HPML with a K_2CrO_4 and Na_2CO_3 solution filter[12] and a Toshiba UVD33S glass filter. Under these experimental conditions, only the sensitizers (DCA and TPT) could absorb the light, since **1a**, **1b**, **1c**, and **1d** had no absorption band at a wavelength longer than 380 nm, whereas in the case of DCN sensitization, more than 98% of the light was absorbed by DCN. After the decomposition monitored by HPLC (silica gel, eluent; hexane:AcOEt = 85:15 by volume, flow rate; 2.0 cm^3 min^{-1}) was complete, the yields of **2** and **3** were determined by GC analysis (OV 17–3 m, column temperature; 170 °C).

Product Analysis. Product isolation was carried out by an appropriate method and the structure was determined from the analytical data. Some products had a very low yield. The values of the yields are isolated yields. Details are described below.

Isolation of the Decomposition Products of 1c. The cyclopropane, **2c**, and the olefin, **3c**, were isolated from the DCA-sensitized decomposition of **1c** using a 1-kW mercury arc lamp in a merry-go-round apparatus. **1c** (0.30 g, 1.2 mmol) and DCA (6.0 mg, 2.6 × 10^{-2} mmol) were dissolved in 0.2 L of dry acetonitrile and irradiated at 405 nm with a 1-kW HPML through a $CuSO_4$ + $NaNO_2$ + NH_4OH solution filter for 22 h after nitrogen purging. After concentration of the solution, **2c** (R_f = 0.20) and **3c** (R_f = 0.08) were separated by flash chromatography (silica gel, hexane:AcOEt = 95:5). **2c** was purified by distillation (bp 25 °C/5 mmHg). A clear oil (33 mg, 12%) was obtained: ^1H NMR (270 MHz, $CDCl_3$) δ = 7.11–7.33 (5H, m), 3.74 (3H, s), 2.83 (1H, s), 1.30 (3H, s), 1.13 (3H, s), 1.05 (3H, s). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.96; H, 8.09. The stereochemistry of this compound was determined by ^1H NMR (270 MHz, $CDCl_3$) of **2c** containing a shift reagent (0.33 weight ratio of Eu-DPM to **2c**). Signals at δ = 3.74, 2.83, 1.30, 1.13, and 1.05 were shifted to 4.62, 3.84, 1.91, 1.67, and 1.34, respectively.

3c was purified by distillation (bp 20 °C/5 mmHg). A clear oil (33 mg, 12%) was obtained: ^1H NMR (270 MHz, $CDCl_3$) δ = 7.10–7.30 (6H, m), 3.75 (3H, s), 1.35–1.50 (9H, m); IR (neat) 1720 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.96; H, 8.23.

Isolation of the Decomposition Products of 1a. **2a** was isolated from the thermolysis of **1a**. A 200 mg (0.72 mmol) sample of **1a** was heated at 140 °C under an argon atmosphere for 5 h. Purification of **2a** was carried out by flash chromatography followed by distillation at 90 °C/3 mmHg. A clear oil (71 mg, 39%) was obtained: ^1H NMR (270 MHz, $CDCl_3$) δ = 7.05 (2H, d, J = 15 Hz), 6.84 (2H, d, J = 15 Hz), 3.79 (3H, s), 3.73 (3H, s), 2.75 (1H, s), 1.28 (3H, s), 1.12 (3H, s), 1.03 (3H, s). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.24; H, 8.07.

3a was isolated from the DCN-sensitized decomposition of **1a.** A 0.2 L aliquot of dry acetonitrile solution containing **1a** (0.4 g 1.4 mmol) and DCN (48 mg, 0.27 mmol) was irradiated by a 1-kW HPML for 17 h under a nitrogen atmosphere. After

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removal of the solvent, product mixtures were separated by flash chromatography (silica gel, hexane:AcOEt = 95:5). The obtained **3a** (R_f = 0.21) was purified by distillation at bp 50 °C/3 mmHg. A 8.4 mg (2.3%) product as a clear oil was obtained: ^{1}H NMR (270 MHz, $CDCl_3$) δ = 6.75−7.30 (5H, m), 3.81 (3H, s), 3.75 (3H, s), 1.40−1.47 (9H, m). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.27; H, 7.82

Isolation of the Decomposition Products of 1b. 2b was isolated from the thermolysis of **1b**. A 0.20 g (0.77 mmol) sample of **1b** was heated at 140 °C under an argon atmosphere for 3.5 h. The purification of **2b** was carried out by flash chromatography and recrystallization from hexane. Colorless crystals (62 mg, 31%) were obtained: ^{1}H NMR (270 MHz, $CDCl_3$) δ = 6.90−7.30 (4H, m), 3.73 (3H, s), 2.83 (1H, s), 2.33 (3H, s), 1.29 (3H, s), 1.14 (3H, s), 1.07 (3H, s). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.43; H, 8.60.

3b was isolated from the decomposition of **1b** by DCA sensitization. A 0.2 L sample of dry acetonitrile solution containing **1b** (0.2 g 0.77 mmol) and DCA (5.0 mg, 2.2 × 10^{-2} mmol) was irradiated by a 1-kW HPML which was equipped with a 405 nm filter solution for 21 h after nitrogen purging. After removal of the solvent, the product mixtures were separated by flash chromatography (silica gel, hexane:AcOEt = 98:2) followed by preparative HPLC. The obtained **2b** showed the same ^{1}H NMR spectra as previously described. Further purification of **3b** was carried out by distillation at bp 50 °C/5 mmHg. A 38 mg (21%) sample of the clear oil was obtained: ^{1}H NMR (270 MHz, $CDCl_3$) δ = 6.90−7.30 (5H, m), 3.74 (3H, s), 2.30 (3H, s), 1.25−1.45 (9H, m); HRMS Calcd for $C_{15}H_{20}O_2$: 232.1463, found 232.1460.

Isolation of the Decomposition Products of 1d. The cyclopropane **2d** was isolated from the thermolysis of **1d**. A 154 mg (0.57 mmol) sample of **1d** was heated at 140 °C under vacuum for 22 h. **2d** was purified by distillation at 150 °C/3 mmHg. A clear oil (57mg, 41%) was obtained: ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.31 (2H, d, J = 15 Hz), 7.26 (2H, d, J = 15 Hz), 3.75 (3H, s), 2.84 (1H, s), 1.30 (3H, s), 1.13 (3H, s), 1.04 (3H, s). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.27; H, 7.13; N, 5.86.

Method of Calculation. Calculations were carried out on the EWS-4800 computer at the Computing Center of Yamagata University, and as software, the AM1 method (MOPAC ver. 6)[6] was used. Optimized structures of the ground state pyrazolines and the radical cations were calculated using a restricted and unrestricted Hartree-Fock wave function, respectively.

Results and Discussion

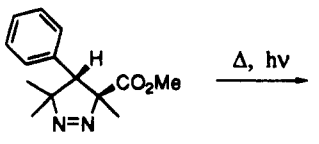
Configuration of Pyrazoline Derivatives. As new derivatives of 3-(methoxycarbonyl)-4-phenyl-3,5,5-trimethyl-1-pyrazoline, **1c**, 4-(*p*-methoxyphenyl)-, 4-(*p*-methylphenyl)-, and 4-(*p*-cyanophenyl)pyrazolines, **1a**, **1b**, and **1d**, respectively, were synthesized from the corresponding methyl α-methyl-*para*-substituted-cinnamate derivatives[13] and 2-diazopropane[14] as previously reported.[7] The X-ray diffraction[8] and ^{1}H NMR spectra containing a shift reagent reveals that the pyrazoline, **1c**, has a stereochemistry in which the aryl group takes a trans junction against the 3-(methoxycarbonyl) group; *r*-3-(methoxycarbonyl)-*t*-4-phenyl-3,5,5-trimethyl-1-pyrazoline. Also, the similarity in the ^{1}H NMR spectra of all the examined pyrazolines reveals that they have the same stereochemistry. This identified structure is reasonable because it is derived from the 1,3-cycloaddition reaction between the cinnamate and the diazopropane.[15]

Thermolysis, Direct Photolysis, and Benzophenone-Sensitized Photolysis of Pyrazoline, 1c. The pyrazoline was decomposed under various conditions, and the product yields were determined. From the thermolysis of neat **1c** at 140 °C under vacuum, only the cyclopropane derivative, **2c**, was isolated. The structure was determined by ^{1}H NMR with a shift reagent. The chemical shifts showed a tendency similar to those of the ^{1}H NMR of **1c** containing the shift reagent. Upon direct photolysis and benzophenone-sensitized photolysis, the main product had the same stereochemistry as that derived by thermolysis. Though only a trace amount of products, which the GC−MS showed to have the same molecular weight as **2c**, were observed in these experiments, the yields were too low to determine whether or not they were the stereoisomer of **2c**. Except for the benzophenone-sensitized decomposition of **1c**, an olefin derivative, **3c**, was detected by the gas chromatography. However, the formation was too low to determine the yield.

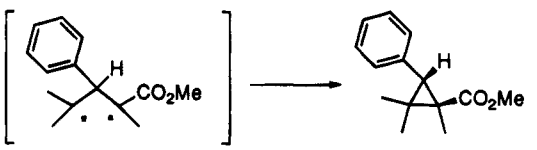
Table 1. Direct and Triplet-Sensitized Photolysis and Thermolysis of 1c

	yield[a] (%)		
	thermolysis[b] at 140 °C	photolysis	
		direct[c]	BP sens[d]
2c	74	66	90
3c	trace	trace	none

[a] Conversions are 100% in all experiments. [b] In vacuo, neat **1c** was heated for 3.5 h. [c] Irradiated at 366 nm light for 3.5 h in acetonitrile. [d] Irradiated at 366 nm light for 3 h in the presence of benzophenone (0.028 M) in acetonitrile.



1c



2c

It has been reported that the decomposition of 1-pyrazolines gave 1,3-biradical intermediates with the loss of nitrogen.[16] The radical centers immediately recombined to afford the corresponding cyclopropyl compounds. It is certain that **1c** reacts via the usual pathway during both thermolysis and direct photolysis as shown in Table 1.

In the presence of benzophenone (BP, E_T = 69 kcal mol^{-1}), **1c** was efficiently decomposed in acetonitrile. However, 9-fluorenone (E_T = 54 kcal mol^{-1}) could not sensitize the decomposition of **1c**. Phosphorescence or transient absorption of **1c** was not observed as in the cases of the other azoalkanes.[17] On the basis of the

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Table 2. Quenching Rate Constants of Sensitizers by Pyrazoline Derivatives

	k_q (M^{-1} s^{-1})		
	DCA[a]	DCN[a]	TPT[b]
1a	7.7×10^9	4.4×10^{10}	2.4×10^{10}
1b	4.9×10^8	3.3×10^{10}	2.0×10^{10}
1c	1.3×10^8	2.7×10^{10}	1.2×10^{10}
1d	7.4×10^7	3.1×10^{10}	6.5×10^9

[a] In acetonitrile under argon. [b] In CH_2Cl_2 under argon.

results of these triplet sensitization reactions, the triplet excited state of **1c** must lie between 54 and 69 kcal mol^{-1} like the other azoalkanes,[18] and the behavior of **1c** can be explained by a normal energy transfer mechanism. The triplet-sensitized reaction of **1c** gave the cyclopropane, **2c**, in excellent yield (Table 1). This means that the benzophenone-sensitized reaction is cleaner than the direct photolysis and the thermolysis, because the starting materials were entirely decomposed in all experiments. In contrast, it is reported that the triplet-sensitized decomposition of pyrazoline gave a mixture of the stereoisomeric cyclopropanes, one of which was produced by direct photolysis.[19] This means the product distributions are affected by the difference in the spin states of the generated biradicals. But it was a fact that only one isomer, **2c**, was predominantly provided from all the previously described decompositions of **1c**. It suggests that a stereochemically favored product is produced in spite of the difference in the spin state (singlet or triplet) of the biradical intermediates.

Fluorescence Quenching of Singlet Excited Sensitizers by Pyrazolines. The fluorescence of the sensitizers, DCA, DCN, and TPT, was quenched by the pyrazolines in acetonitrile or dichloromethane, and the quenching rate constants, k_q, were calculated from the Stern–Volmer constants, $k_q\tau_S$, and the lifetimes of the singlet excited sensitizers, τ_S. The lifetimes of DCA, DCN, and TPT were 16,[20] 10,[21] and 2.7 ns,[9] respectively. These results are summarized in Table 2. In contrast to the k_q's of DCN and TPT, which are as fast as the diffusion rate constants, those of DCA are slow, especially in the case of **1b-d**. Furthermore, we studied the quenching of the sensitizer fluorescence using benzonitrile which corresponds with only the aryl moiety of **1d**. The quenching rate constants of DCA and DCN, 6.9×10^6 and 5.5×10^6 M^{-1} s^{-1}, respectively, are quite slower than those obtained for **1d**. To explain the results in Table 2, the Rehm–Weller correlation was examined between the pyrazolines and the excited singlet sensitizers. For oxidation potential, E^{ox}, during measurement of the pyrazolines, irreversible waves were observed and the E^{ox} values of **1a**, **1b**, **1c**, and **1d** were determined to be 1.60, 1.87, 1.95, and 1.97 V vs SCE, respectively. On the other hand, the reduction potentials, E^{red}, of the excited sensitizers, $E^{red} + E_{0,0}$ (where $E_{0,0}$ indicates the singlet excitation energies obtained from their fluorescence 0,0 band), of DCA, DCN, and TPT are 1.97, 2.17, and 2.53 V vs SCE, respectively.[22] In the cases of DCN and TPT, the ΔG values derived from Rehm–Weller's

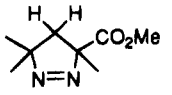
Table 3. Free Energy Change, ΔG, between Sensitizers and Pyrazoline Derivatives

	ΔG^a (kcal mol^{-1})		
	DCA	DCN	TPT
1a	−9.2	−13.8	−22.1
1b	−3.0	−7.6	−15.9
1c	−1.2	−5.8	−14.1
1d	−0.7	−5.3	−13.6

[a] Derived from Rehm–Weller's equation, $\Delta G = E^{ox} - E^{red} - E_{0,0} - e_0^2/\epsilon_a$.

equation,[23] $E^{ox} - E^{red} - E_{0,0} - e_0^2/\epsilon_a$ (a Coulomb term, e_0^2/ϵ_a, = 0.7 kcal mol^{-1} in acetonitrile[24]), are more negative than −5.3 kcal mol^{-1} as shown in Table 3, and all the values of k_q nearly equal the diffusion rate constants for every pyrazoline. However, in the series of DCA with the pyrazolines except **1a**, the ΔG values are only slightly negative, because of the small reduction potential of the excited DCA. Also, the k_q of DCA by **1d** is much slower than the diffusion rate constant (Table 3). These results show good correlation between the k_q and the ΔG which were derived from the redox potentials of the singlet excited states of the sensitizers and the pyrazolines.

It was confirmed that the process of PET proceeds efficiently in this reaction; however, it is still uncertain which electron of the pyrazoline, **1**, that of the aryl site or that of the azo site, is involved in the initial PET process. Therefore, the oxidation potentials of the fragment molecules of **1** such as anisole and 3-(methoxycarbonyl)-3,5,5-trimethyl-1-pyrazolines, **4**,[16] were measured



4

as 1.56 and 2.05 V vs SCE, respectively. The E^{ox} of **4** is more positive than those of **1a-c** and that of anisole is quite similar to that of **1a**. In contrast, the E^{ox} of **1d** is similar to that of **4** but more negative than that of benzonitrile which was reported as 2.74 V vs SCE.[25] It was a fact that the fluorescence quenching of DCA by benzonitrile was less efficient than that of **1d**. It suggests that the first oxidized positions of **1a-c** are in the aryl moiety, whereas **1d** is initially oxidized at the azo moiety.

Such considerations are also supported by a comparison of ionization potentials of the fragment compounds of **1**. The values of the vertical ionization potential, $(Ip_v)_{obsd}$, measured by ultraviolet photoelectron spectroscopy (VUV-PES) of anisole, toluene, benzene, and benzonitrile are reported as 8.39,[26] 8.85,[26] 9.24,[27] and 9.72 V,[26] respectively. In additon, the $(Ip_v)_{obsd}$ of **4**, reported

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(20) This value was determined in this work. Literature values are 15.3 ns and 19.6 ns. The former is in: Eriksen, J.; Foote, C. S. *J. Phys. Chem.* **1978**, *82*, 2659. The latter is in: Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

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Table 4. Relative Rates of Decomposition and Quantum Yields of DCA Sensitization Reaction of 1a-d in Acetonitrile

	k_{rel}[a]	Φ_{obs}[b]	Q_{ratio}[c]	Φ_{dec}
1a	1.8	1.3×10^{-2}	0.55	0.024
1b	1.7	1.2×10^{-2}	0.072	0.17
1c	1	7.2×10^{-3}	0.020	0.36
1d	0.46	3.3×10^{-3}	0.012	0.28

[a] At 0.01 M of **1**. [b] Determined at <5% conversion of 0.01M of **1**. [c] $k_q[\mathbf{1}]/(k_d + k_q[\mathbf{1}])$.

by Houk et al. as 8.94 V,[28] shows that the pyrazolinyl moiety itself is less oxidative than the anisyl moiety and more oxidative than the *p*-cyanophenyl moiety. An ambiguity of the oxidation ability among the tolyl, phenyl, and pyrazolinyl moieties will be clarified by the molecular orbital considerations to be discussed later.

Kinetic Parameters on PET Decompositions of Pyrazolines. The decomposition quantum yields (Φ_{dec}) of the intermediate radical cations of the pyrazolines (**6a**$^{\cdot+}$ or **7a**$^{\cdot+}$) were determined by DCA sensitization. In the presence of DCA (0.23 mM), **1a-d** (10 mM) were decomposed by 366 nm light in acetonitrile, and the observed decomposition quantum yields, Φ_{obs}, were determined by HPLC and a ferrioxalate actinometer. The relative decomposition rates, k_{rel}, of **1a**, **1b**, and **1d** versus **1c** were determined by 366 nm light in a merry-go-round apparatus at the same concentrations of DCA (0.23 mM) and each pyrazoline (10 mM). The real decomposition quantum yields, Φ_{dec}, are evaluated from Φ_{obs} and the quenching ratio, Q_{ratio} ($\Phi_{dec} = \Phi_{obs}/Q_{ratio}$). In this equation, Q_{ratio} indicates the quenching efficiency of the excited singlet state of DCA under the same concentration (10 mM) of **1a-d**, $Q_{ratio} = k_q[\mathbf{1}]/k_d + k_q[\mathbf{1}]$, where k_d is the decay rate of the excited singlet state of the sensitizer ($k_d = \tau_S^{-1}$). These values are listed in Table 4. Upon quenching of the DCA fluorescence by the pyrazolines, **1a** showed the largest k_q values, in contrast, the smallest k_q was observed for **1d** (Table 4). The Q_{ratio} indicates that only 1−2% of the fluorescence of DCA was quenched by **1d** or **1c**, while **1a** quenched more than 50% of the DCA fluorescence. The Φ_{dec} derived from Φ_{obs} and Q_{ratio} must reflect the stability of the radical cations which should be responsible for the difference in the reactivity of **1a-d**. The smallest Φ_{dec} of **1a** means that the decomposition efficiency (total conversions available) of the radical cation, **6a**$^{\cdot+}$ or **7a**$^{\cdot+}$, is minimal even though the observed overall reaction quantum yield, Φ_{obs}, is maximal. This is caused by an efficient back-electron transfer to the stable radical cation, **1a**$^{\cdot+}$, from the anion radicals of the sensitizer.[29] On the contrary, though the Q_{ratio} of **1c** and **1d** are quite small, the generated radical cations could efficiently decompose. The rapid reaction of the unstable radical cation should make the back-electron transfer process negligible.

PET Decompositions of Pyrazolines, 1a-d. During some PET decompositions in acetonitrile of **1** by DCA, DCN, and TPT, the olefins **3** were produced with **2**. DCA, DCN, and TPT are well-known electron-accepting sensitizers. The olefins, **3**, are quite unique rearrangement products, and they are the primary products of the PET reactions of **1**'s because no reaction occurred under the same reaction conditions of the cyclopropanes, **2**'s. Furthermore, it should be noticed that, during the PET decompositions of **1a-d**, product distributions are dramatically changed based on the difference in *para*-substituents of the phenyl moiety of **1**'s. The results are shown in Table 5. The pyrazoline, **1a**, which has an electron-donating substituent such as the methoxy group, produced mainly the olefin derivative, **3**, whereas the cyclopropane, **2**, was exclusively afforded from the pyrazoline bearing an electron-withdrawing group such as the cyano group, **1d**. The pyrazolines, **1b** and **1c**, which have the *p*-methyl and hydrogen aryl moieties, respectively, showed the competitive formation of **2** and **3**.

Table 5. Product Yield of Photoinduced Electron Transfer Reaction[a] of 1a-d in Acetonitrile

		products yield[b] (%)	
substrate	sensitizer	**2**	**3**
1a	DCA[c]	12	60
1a	DCA[d]	17	76
1a	TPT[c]	trace	61
1b	DCA[c]	33	44
1b	DCN[d]	35	38
1b	TPT[c]	3	48
1c	DCA[c]	42	25
1c	DCN[d]	53	23
1c	TPT[c]	13	25
1d	DCA[c]	79	trace
1d	DCN[d]	86	trace
1d	TPT[c]	53	trace

[a] See Experimental Section for reaction conditions. [b] Conversions are 100% in all experiments, and yields were determined by GC. [c] Irradiated under 405 nm light. [d] Irradiated under 313 nm light.

Table 6. Some Parameters of the Pyrazolines and the Fragment Compounds

compd	**1a**	**1b**	**1c**	**1d**	**4**
E^{ox}[a]/eV	1.60	1.87	1.95	1.97	2.05
$(Ip_a)_{calcd}$[b]	8.30	8.69	8.97	9.27	8.86
compd	PhOMe	PhMe	PhN	PhCN	4
$(Ip_v)_{obsd}$[c]	8.39	8.85	9.24	9.72	8.94

[a] Vs SCE. Measured by cyclic voltammetry in dry CH_3CN. [b] Adiabatic ionization potentials are evaluated by difference of the heats of formation between the neutral and the radical cation which are optimized by AM1 calculations, respectively. [c] Vertical ionization potentials of PhOMe,[26] PhMe,[26] PhH,[27] PhCN,[26] and **4**[28] were reported as the results of photoelectron spectroscopy.

Semiempirical Molecular Orbital Calculations of Ground States and Radical Cations of 1a-c and 4. During the PET reaction, the pyrazoline, **1d**, may decompose through a direct electron transfer from the azo moiety, because the E^{ox} and $(Ip_v)_{obsd}$ of the *p*-cyanophenyl moiety are more positive than those of the pyrazolinyl moiety. The PET reactions of **1a-c** afforded the cyclopropanes and the olefins with different distributions. Therefore, for the pyrazolines, **1a-c** and **4**, to get insight into the quantitative information of the ground state neutral species and the radical cations, semiempirical MO calculations were carried out by RHF− and UHF−AM1 optimizations, respectively.[6] At first, the ionic potential of **4** was evaluated as 8.86 V by the gap of the heats of formation between the optimized neutral **4** and the optimized cation radical, **4**$^{\cdot+}$. Though the evaluated value corresponds to an adiabatic ionization potential, $(Ip_a)_{calcd}$, its validity is supported by a good correlation with the $(Ip_v)_{obsd}$ of **4**, 8.94 V, shown in Table 6. The values of $(Ip_a)_{calcd}$ of **1a-c**, given by the same manner as previously stated, show good correlations with those of $(Ip_v)_{obsd}$ of the corresponding fragment compounds (Table 6).

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(29) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

Table 7. Geometrical Parameter of Neutral and Radical Cation of 1a-c by AM1 Calculation[a] and of X-ray Data of 1c Crystal

	1a	1b	1c	X-ray data of 1c
distance[b]				
N-1, N-2	1.243 (1.208)	1.235 (1.207)	1.241 (1.207)	1.233
N-1, C_{ipso}	3.540 (3.497)	3.540 (3.489)	3.539 (3.480)	3.457
N-2, C_{ipso}	3.545 (3.500)	3.545 (3.494)	3.545 (3.487)	3.468
N-1, C_{ortho}	4.796 (4.797)	4.797 (4.791)	4.796 (4.787)	4.733
N-2, C_{ortho}	4.797 (4.796)	4.800 (4.798)	4.799 (4.798)	4.745
N-1, $C_{ortho'}$	3.833 (3.766)	3.835 (3.759)	3.832 (3.746)	3.698
N-2, $C_{ortho'}$	3.842 (3.711)	3.843 (3.762)	3.841 (3.746)	3.697
C-3, C_{ipso}	2.581 (2.564)	2.582 (2.562)	2.582 (2.561)	2.592
C-4, C_{ipso}	1.485 (1.476)	1.486 (1.471)	1.486 (1.466)	1.501
C-5, C_{ipso}	2.594 (2.583)	2.593 (2.576)	2.593 (2.572)	2.607
angle				
N-1, N-2, C_{ipso}	79.94 (79.89)	79.92 (79.80)	79.92 (79.73)	79.24
N-2, N-1, C_{ipso}	80.41 (80.23)	80.42 (80.29)	80.42 (80.33)	80.25
N-1, C_{ipso}, $C_{ortho'}$	91.08 (89.55)	91.26 (89.42)	91.14 (89.06)	88.60
dihedral angle				
N-2, N-1, C-4, H_{C-4}	99.03 (99.70)	99.05 (99.75)	99.06 (99.82)	
C_o, C_i, $C_{o'}$, $C_{m'}$	0.07 (0.27)	0.02 (0.46)	0.04 (0.78)	
H_{C-4}, C-4, C_i, C_p	2.18 (11.03)	2.33 (17.52)	2.40 (17.52)	
N-2, N-1, C_i, C_p	106.80 (104.91)	106.89 (104.97)	106.89 (104.70)	
N-2, N-1, C_i, C_o	105.50 (106.65)	105.90 (108.83)	105.82 (110.31)	
N-2, N-1, C_i, $C_{o'}$	90.76 (90.24)	90.65 (89.59)	90.62 (89.15)	88.41

[a] The values in parentheses are those of radical cation of **1**. [b] In angstroms.

At the next stage, some geometrical parameters of the optimized structures of both the neutrals and the radical cations of **1a-c** are shown in Table 7. Validity of the optimized structure of the neutral **1c** was checked by a comparison with that of the X-ray data which are also listed in Table 7. Characteristic stereochemical properties are listed as follows: (1) All the radical cations **(1a-c)**$^{\cdot+}$, have a shorter N1−N2 bond length of about 3 pm than those of the neutral **1a-c**. (2) All the five membered rings of the pyrazolines have a conformation like an envelope in which the atoms of C3, N2, N1, and C5 lie on a plane and the atom C4, having a quasi-axial aryl ring, takes a slightly folded position. (3) The distances between the atoms C*i* and N1 or N2 are nearly equidistant in each case of the neutrals **1a-c** and the radical cations **(1a-c)**$^{\cdot+}$, respectively. (4) The distances of the atoms C*i*−N1 or C*i*−N2 of **(1a-c)**$^{\cdot+}$ are shorter than those of **1a-c**; on the average, 349 pm for **(1a-c)**$^{\cdot+}$ and 354 pm for **1a-c** are given. (5) Whether the pyrazolines are neutral or radical cations, they have a similar conformation in which the aryl ring is nearly orthogonal to the pyrazolinyl plane. The orthogonal aryl plane contains a vertical bisector of the isosceles triangle drawn by the atoms C*i*, N1, and N2. The asymmetrical *ortho* carbons of the aryl ring are then distinguished as C*o* and C*o*', which exist on the exo (far) and endo (near) side of the pyrazolinyl ring, respectively. The *meta* carbons are also treated in the same manner (Figure 1).

From these experimental and calculated results, we should consider the through-space interaction between the aryl π orbital and b_2 nonbonding orbital of the N1−N2 bond[28] of the pyrazolinyl moiety, even though the aryl ring and pyrazolinyl plane are orthogonal to each other. Generally, in neutral **1**, each aryl π orbital and b_2 nonbonding orbital of N1−N2 have two electrons. Thus, the through-space interaction of the neutral **1**, according to the perturbation theory, causes a destabilization because of the two-orbital-four-electron interaction. In contrast, a significant amount of stabilization would be expected for the radical cation, **1**$^{\cdot+}$, since the two-orbital-three-electron interaction could operate. Furthermore, from the stereochemical properties of the radical cations, both C*i* and C*o*' of the aryl moiety are responsible for

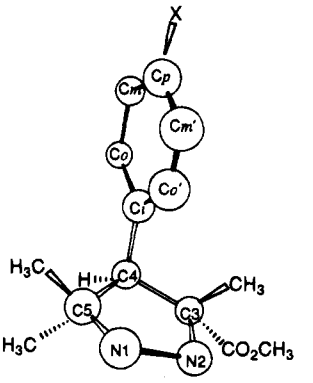

Figure 1. *r*-3-(Methoxycarbonyl)-*t*-4-(*para*-substituted-phenyl)-3,5,5-trimethyl-1-pyrazolines **1**: **1a**, X = MeO; **1b**, X = Me; **1c**, X = H; and **1d**, X = CN. This figure is obtained from the X-ray diffraction of **1c**.

the stabilization with the nonbonding orbital of N1 and N2. Among the aryl carbons, the C*i* exists at the position nearest to both the nitrogen atoms as 350 pm. Since the value of an overlap integral of 2pσ(C−N/350 pm) is calculated as 0.27 eV,[30] the electronic character at the C*i* should affect the properties of the radical cations.

Therefore, the electronic properties of the optimized radical cations **(1a-c)**$^{\cdot+}$, were also investigated. At first, the population of the positive charge at the aryl site and that of the pyrazolinyl site are separately shown in Table 8. A predominant population of the charge at the aryl moiety is observed for **(1a-c)**$^{\cdot+}$, though as the ability of electron donation of the *para*-substituent is reduced, a lower positive charge value at the aryl site is observed. Next, the spin electron population is also shown in Table 8. Predominancy of the spin electron population at the aryl site of **(1a-c)**$^{\cdot+}$ is also observed as in the case of the positive charge of **(1a-c)**$^{\cdot+}$. It suggests that the neutrals **1a-c** are initially oxidized at the aryl moiety. Furthermore, for each position of the aryl site and the pyrazolinyl site of **(1a-c)**$^{\cdot+}$, the changes in the charge from the

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Table 8. Some Parameters of the Radical Cation of 1a-c by MO (AM1) Calculation

	1a	1b	1c
charge[a]			
aryl site	+0.858	+0.830	+0.801
pyrazolinyl site	+0.142	+0.170	+0.199
Δ charge[b]			
aryl site; C_{ipso}	+0.171*	+0.207*	+0.232*
C_{ortho}	+0.028	+0.009	+0.002
C_{meta}	+0.032	+0.058	+0.052
$C_{ortho'}$	+0.002	+0.039	+0.057
$C_{meta'}$	+0.055	+0.010	−0.001
C_{para}	+0.302*	+0.189*	+0.171*
pyrazolinyl site; N-1	+0.029	+0.028	+0.031
N-2	+0.024	+0.033	+0.036
C-3	+0.005	+0.009	+0.013
C-4	−0.068	−0.082	−0.093
C-5	+0.013	+0.018	+0.024
spin density[c]			
aryl site	0.984	0.962	0.939
pyrazolinyl site	0.016	0.038	0.061
aryl site; C_{ipso}	0.572*	0.482*	0.433*
C_{ortho}	−0.207	−0.060	0.049
C_{meta}	0.248	0.066	−0.055
$C_{ortho'}$	−0.280	0.022	0.214
$C_{meta'}$	0.309	−0.023	−0.120
C_{para}	0.152	0.439*	0.532*
pyrazolinyl site; N-1	0.002	0.004	0.007
N-2	0.001	0.002	0.003
C-3	0.034	0.036	0.041
C-4	−0.053	−0.043	−0.036
C-5	0.032	0.036	0.042

[a]Charge of the radical cation of 1. [b]Charge difference at each atom is calculated by subtraction: $(charge)_{radical\ cation} - (charge)_{neutral}$. [c]Spin density of the radical cation of 1.

neutrals to the radical cations and the values of the spin electron populations are investigated. Upon comparison of both changes in charge and the spin electrons of the radical cations **(1a-c)**$^{\cdot+}$, it becomes clear that the distribution of a cation and a radical in the aryl moiety is quite different between the radical cations **(1a-c)**$^{\cdot+}$ (Table 8). In **1a**$^{\cdot+}$, the positive charge at the *ipso* position is small, but large at the *para* position of the aryl moiety. On the contrary, the spin density at the *ipso* position is more than three times that at the *para* position. Both the charge difference and the spin population of **1b**$^{\cdot+}$ are nearly equal at the *ipso* and the *para* positions, respectively. In the case of **1c**$^{\cdot+}$, the spin population of the *para* position is larger than that of the *ipso* position, and the positive charge at the *ipso* position is relatively high.

Reaction Scheme of PET Decompositions of 1a-d. It is obvious that the *para*-substituents affect the product distributions on the PET decompositions of **1a-d**. When an electron-donating group is substituted at the phenyl moiety, the yield of olefin is high and decreases in the order of **1a** > **1b** > **1c** > **1d**. A reversed tendency is observed in the yields of the cyclopropane. From the MO considerations of **1**$^{\cdot+}$, it suggests that the location of the positive charge and spin electron controls the product distribution. When the spin electron is mainly located at the *ipso* position of the aryl ring where it is next to the pyrazolinyl ring, the olefin is predominantly produced. A diminution in the radical at *ipso* position, in which the positive charge at *ipso* position is alternatively enhanced, caused an attenuation of the olefin production.

On the basis of these results, **1d** may directly decompose through an electron transfer from the azo chromophore, because the oxidation potential of the *p*-cyanophenyl moiety is more positive than that of the azo chromophore. This is path A in which the azo radical cation **5**$^{\cdot+}$ is directly generated as shown in Scheme 1. The derived radical cation, followed by the nitrogen elimination and the back-electron transfer from the radical anion of sensitizer, exclusively produced the cyclopropane, **3**. The mechanism of bond cleavage to generate a diazenyl cation and a carbon radical in other azo compounds was reported by Adam et al.[5] The mechanism of bond cleavage of the pyrazolinyl radical cation is now investigated by MO calculations for the N1−C5 or N2−C3 cleavage of **5**$^{\cdot+}$.

On the other hand, the radical cations **(1a-c)**$^{\cdot+}$, after an electron is removed from the aryl site, may have a resonance between **6**$^{\cdot+}$ and **7**$^{\cdot+}$. In the case where a radical is mainly located at the *ipso* position, **6**$^{\cdot+}$, along path B, a S_H2 displacement between the C*i* and C5 occurs to cleave the C5−N1 bond and to produce a spiro intermediate, **8**$^{\cdot+}$. After the elimination of nitrogen, the generated cyclopropyl cation radical is then rapidly rearranged to an olefin cation radical by a cyclopropylcarbinyl rearrangement. Finally, the olefin **3** is formed by the back-electron transfer from the radical anion sensitizer. This migration of the aryl moiety is similar to the electrochemical oxidation reaction of the aromatic alkenes.[31] In contrast, there is a large positive charge at the *ipso* position, **7**$^{\cdot+}$; the 1,2-migration cannot occur and the reaction proceeds via path C in Scheme 1. In this case, an electron transfers from the azo moiety to the phenyl radical cation site and an azo radical cation, **5**$^{\cdot+}$, is generated, though this process may be an endothermic process. After the elimination of nitrogen and the back-electron transfer, the derived 1,3-biradical exclusively afforded the cyclopropane, **2**.

On the basis of the calculated results of the charge and the spin density of the radical cations, it is proposed that the **1a**$^{\cdot+}$-type radical cation decomposes via path B to give the olefin and the **1c**$^{\cdot+}$-type decomposes via path C to give the cyclopropane, respectively. In the case of **1b**$^{\cdot+}$, a comparable population of the charge and the spin density at the *ipso* position indicates a parallel production of the olefin and the cyclopropane. The product distribution is in good correlation with this postulation. Furthermore, the reason for the difference in the product distributions can be rationalized to the difference in the orbital interactions of the radical cations between **6**$^{\cdot+}$ and **7**$^{\cdot+}$. The radical cation, **7**$^{\cdot+}$, could afford the large two-orbital-less-three-electron stabilization because of its spin vacancy at the C*i* position. An electron transfer from the azo moiety to the aryl site could then easily occur to give **5**$^{\cdot+}$. In contrast, the radical cation **6**$^{\cdot+}$, having a high spin population at the C*i* position, produces less stabilization. It should be difficult to transfer an electron from the azo moiety to the aryl site to give **5**$^{\cdot+}$. This is the reason why the efficiency of the back-electron transfer of **1a**$^{\cdot+}$ is higher than the others. As a minor process, the bridging of the aryl moiety to the C5 position could produce a vacancy at the C4 position, which should cause the 2-orbital-2-electron stabilization at the pyrazolinyl site. The stabilization energy should be responsible for the driving force of the aryl migration. We confirmed that this reaction proceeds through the mechanism described above.

The product yields of the TPT sensitizations are lower than those of the DCA and DCN sensitizations. This tendency has sometimes been observed in other experi-

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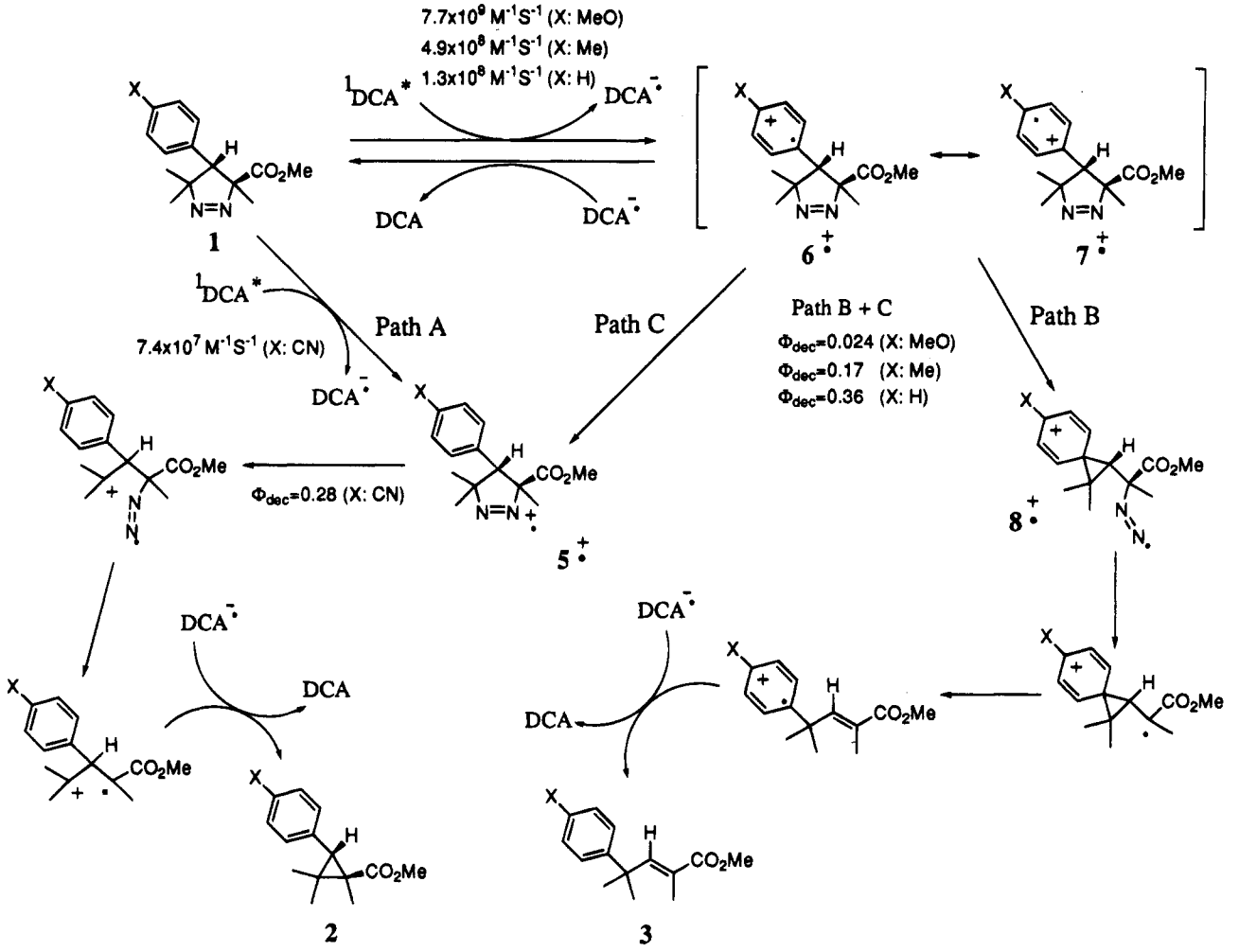
Scheme 1



ments.[5] TPT is a favorite sensitizer in a photoinduced electron transfer reaction because it leads to good charge separation.[32] In this experiment, TPT fluorescence almost disappeared after the irradiation. The low yield may be attributed to the reaction between the pyranyl radical and a pyrazoline or an intermediate which is produced from a pyrazoline by the PET reaction,[33] or the polymeric reaction of the cationic species generated by the better charge separation of TPT than DCA, even though no detectable products were observed by GC. In addition, the 1,2-radical cation must be less reactive than the 1,3-radical cation by cationic polymerization, because the large steric bulkiness results in higher yields of **3** than of **2** in the case of the TPT sensitization.

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Conclusions

The specific product is obtained during the PET decomposition of the 1-pyrazoline, and the mechanism of the initial process is clearly explained. We report the stability of the intermediate radical cation and the position of a radical and a cation which play an important role in reaction efficiency and product distribution. Under these considerations, we are able to determine reactions to obtain characteristic products by the PET reaction and to clarify the reaction mechanisms.

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