Bull. Chem. Soc. Jpn., ***69***, *3325—3329 (1996)*

Photoinduced Electron-Transfer Reaction of (Phenylazo)triphenylmethane (PAT). Behavior of Generated Trityl Cation

Nobukazu Miyagawa,† Takashi Karatsu,* Yasuo Futami, Takeshi Kunihiro, Atsushi Kiyota, and Akihide Kitamura*

Department of Materials Science, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba 263

†Graduate School of Science and Technology, Chiba University, Yayoi-cho, Inage-ku, Chiba 263

(Received June 17, 1996)

The decomposition mechanism of photoinduced electron transfer (PET) between electron deficient sensitizers and (phenylazo)triphenylmethane (**PAT**) was investigated. In 9,10-dicyanoanthracene (**DCA**) sensitized reaction, benzene, triphenylmethane, 3,3,3-triphenylpropionitrile, and [4-(diphenylmethyl)phenyl]acetonitrile were obtained, and the product distribution was the same as for the direct photolysis and the thermolysis. In the case of 2,4,6-triphenylpyrylium tetrafluoroborate (**TPP**$^+$) sensitization, the product distribution was drastically changed and 9-phenylfluorene was found to be one of the main products. The results of the irradiation wavelength effects indicate that 9-phenylfluorene is produced by the photoreaction of a trityl cation which is generated by the decomposition of a radical cation of **PAT**. The results of the experiments of laser flash photolysis suggest that the rate of back electron transfer between a radical anion of the sensitizer and a trityl cation plays an important role in these reactions.

Ground state charge-transfer reactions (CT) of (phenylazo)triphenylmethane (**PAT**) have been investigated and 74% yield of triphenylmethanol was obtained by the addition of water to the reaction solution.[1] However, photoinduced electron-transfer (PET) reaction of **PAT** has not yet been reported, though PET reactions of azoalkane have been extensively studied in recent years.[2] Characteristic products by the PET reaction have probably not been obtained, since the product distribution of the PET reaction is similar to that of the direct photolysis. No difference of the product distribution between PET reaction and direct photolysis has been also observed in the case of the reaction of dibenzoyl peroxide (**DBO**) which is a well-known radical-generating reagent like **PAT**.[3]

In this paper, we report that in 2,4,6,-triphenylpyrylium tetrafluoroborate (**TPP**$^+$) sensitization, the product distribution of **PAT** decomposition is different from that of the direct photolysis, although the sensitization using 9,10-dicyanoanthracene (**DCA**), an electron-deficient sensitizer like **TPP**$^+$,[4] results in the same product distribution as that of the direct photolysis. We examined the transient absorption spectra and observed trityl (triphenylmethyl) cation in the **TPP**$^+$ sensitization, but could not observe it in the **DCA** sensitization. These results indicate that the rate of back electron transfer from the generated radical anion of the sensitizer to the intermediate, trityl cation, which was induced from **PAT**, plays an important role in these reactions. Furthermore, it is supposed that the generated trityl cation absorbed light and cyclized to form 9-phenylfluorene (**2**), which was one of the main products of **TPP**$^+$ sensitized reaction of **PAT**. We carefully examined the product yields and the wavelength effects of irradiation light, and the decomposition mechanism of PET reaction of **PAT** is confirmed.

Experimental

Materials. The sensitizers were purified by recrystallization. Dehydrated acetonitrile (Kanto Chemical Co.) and spectrophotomeric grade dichloromethane (Dotite Co.) were used in photochemical studies. **PAT** was synthesized in the previous manner.[5] Authentic samples, *N*-(triphenylmethyl)acetamide[6] and 3,3,3-triphenylpropionitrile (**3**)[7] were synthesized, [4-(diphenylmethyl)-phenyl]acetonitrile (**4**) was isolated from the photochemical reaction mixture as described below; others were purchased.

Fluorescence Quenching Studies. The quenching rate constants (k_q) of the fluorescence of the sensitizers, **DCA** and **TPP**$^+$, by **PAT** were determined by a Stern–Volmer type plot of the fluorescence lifetime versus the concentration of **PAT**. The lifetime of **DCA** was measured in acetonitrile and that of **TPP**$^+$ was measured in CH_2Cl_2 in the presence of **PAT** under an argon atmosphere. Fluorescence lifetimes of **DCA** and **TPP**$^+$ were measured by the single photon counting method (Horiba NAES-1100). The values are 16 and 2.7 ns, respectively, in the absence of **PAT**.[2e]

Oxidation Potential of PAT. Oxidation potential of **PAT** (10 mM, $M = mol\ dm^{-3}$) was measured by cyclic voltammetry (BAS CV-1B) at a platinum electrode in argon-saturated dry acetonitrile with 0.10 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The scan speed was 200 $mV\ s^{-1}$ and the reference electrode was the SCE. The obtained peak was irreversible, and the oxidation potential, 1.84 V, was determined from the half-peak potential.

Reactions. PET Reactions: Acetonitrile solutions of 2.1 mM of **PAT** (ε_{405} is 200 $M^{-1}\,cm^{-1}$) and 1.4 mM of **DCA** (ε_{405} is 6.93×10^3 $M^{-1}\,cm^{-1}$) or 2.1 mM of **TPP**$^+$ (ε_{405} is 2.16×10^4 $M^{-1}\,cm^{-1}$) were irradiated for 30 min and 3 h, respectively, at >405 nm with a 1 kW high-pressure mercury lamp (HPML) through a $CuSO_4+NaNO_2$ + aqueous ammonia solution filter,[8] and the solution of 2.1 mM **PAT** (ε_{366} is 73.4 $M^{-1}\,cm^{-1}$) and 2.7 mM **TPP**$^+$ (ε_{366} is 3.10×10^4 $M^{-1}\,cm^{-1}$) was irradiated for 3-h at 366 nm by a 1-kW HPML with a Toshiba UVD36B glass filter to isolate the 366 nm light. Under these experimental conditions, in the case of **TPP**$^+$ sensitization, only **TPP**$^+$ could absorb the light (> 99%), in both 366 nm and > 405 nm light irradiations. But in the case of **DCA** sensitization, more than 95% of the light was absorbed by **DCA**. After the decomposition monitored by HPLC (silica gel, eluent; hexane : AcOEt = 95 : 5 by volume, flow rate; 1.0 $cm^3\,min^{-1}$) had finished, product yields were determined by GC analysis (capillary column; Shimadzu CBP10-M25-025, column temp.; 100—250 °C, elevated temp; 10 $°C\,min^{-1}$. Products were stable under these analysis conditions).

Direct Photolyses: Degassed acetonitrile solutions of **PAT** (2.0 mM) were irradiated for 1 h at > 405 m with a 1 kW HPML through the solution filter or at 313 nm with a 1 kW HPML with a K_2CrO_4 and Na_2CO_3 solution filter.[9] After the decomposition monitored by HPLC had finished, product yields were determined by GC.

Thermolysis: Acetonitrile solution of **PAT** (8.1 mM) was sealed in a glass tube under vacuum and thermolyzed at 60 °C for 24 h. Product yields were determined by GC.

Isolation of [4-(Diphenylmethyl)phenyl]acetonitrile (4). **PAT** (820 mg) in 1 L (L = dm^3) of dry acetonitrile was heated at 60 °C under an argon atmosphere for 15 h. After removal of the solvent, the product mixture was separated by preparative GC (OV-1, 2 m, column temp ; 260 °C). Collected **4** was recrystallized from ethanol. Colorless crystals (44 mg, 7%) were obtained. Mp 101—102 °C. ^{1}H NMR (270 MHz, $CDCl_3$) δ = 7.10—7.40 (14H, m), 5.55 (1H, s), 3.70 (2H, s). IR (CCl_4) 2310 cm^{-1} (ν_{CN}). HR MS. Calcd for $C_{21}H_{17}N$: M, 283.1361. Found: *m/z* 283.1348.

Transient Absorption Measurements. Acetonitrile solutions of **PAT** (1.4×10^{-2} M) in the presence of **TPP**$^+$ (8.9×10^{-5} M) or **DCA** (1.2×10^{-4} M) were purged with argon and the transient absorptions were measured. They were measured on excitation at 355 nm (Continuum SL I-10, 6 ns fwhm, 20 mJ per pulse) with a detection system (Tokyo Instruments) composed of a multichannel diode array (Princeton IRY-512G: 18 ns gate) with a SPEX 270M monochrometer (resolution: 0.3 nm/channel).

Results and Discussion

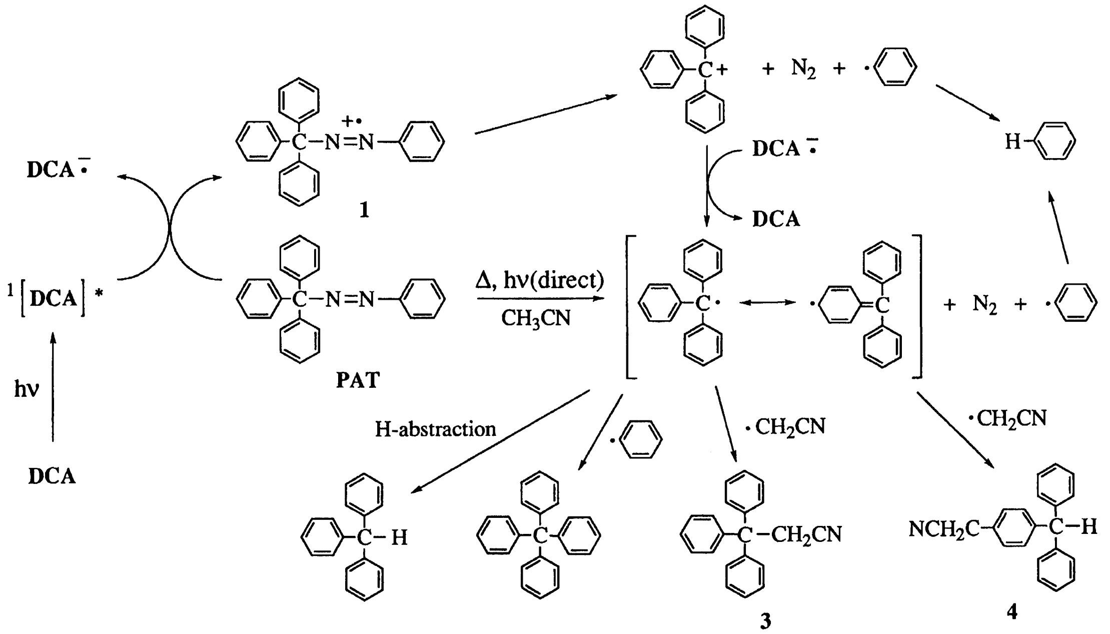
The fluorescence of the sensitizers, **DCA** and **TPP**$^+$, was quenched by **PAT** in acetonitrile or dichloromethane. The quenching-rate constants (k_q) of **DCA** and **TPP**$^+$, were 1.3×10^{10} and 1.8×10^{10} $M^{-1}\,s^{-1}$, respectively. To explain the results, the Rehm–Weller correlation was examined between **PAT** and the excited singlet sensitizers. For oxidation potential, E_{OX}, of **PAT**, irreversible wave was observed and the E_{OX} value was determined to be 1.84 V vs. SCE. On the other hand, the reduction potentials of the excited sensitizers, $E^*_{red}=E_{red}+E_{0,0}$ (where $E_{0,0}$ indicates the single excitation energies obtained from their fluorescence 0,0 band), of **DCA** and **TPP**$^+$ are 1.97 and 2.53 V vs. SCE, respectively.[10] The ΔG values derived from Rehm–Weller's equation,[11] $E_{ox}-E^*_{red}-e_0^2/\varepsilon_a$ (a Coulomb term, e_0^2/ε_a, = 0.7 $kcal\,mol^{-1}$ in acetonitrile,[12] cal = 4.184 J), are negative, −3.7 and −16.6 $kcal\,mol^{-1}$ in the cases for **DCA** and **TPP**$^+$, respectively, and the values of k_q are nearly equal to the diffusion-rate constants. It is confirmed that the processes of PET proceed efficiently in these reactions.

In the presence of **DCA**, **PAT** was photolyzed at > 405 nm light in acetonitrile, and we obtained benzene, **2**, triphenylmethane, tetraphenylmethane, **3**, and **4**. Product yields are shown in Table 1. **DCA** is a well-known electron-accepting sensitizer. The results of the quenching experiment indicate that **PAT** must be decomposed via a radical cation of **PAT** (**1**). The radical cation **1** eliminates nitrogen easily and a phenyl radical and a trityl cation are generated. Obtained benzene in good yield is produced from the phenyl radical, and other products have to derive from the trityl cation. However, these products seem to be provided via trityl radical and their formation mechanisms are clearly explained, except for 9-phenylfluorene (**2**), as shown in Scheme 1. Triphenylmethane is a product from a trityl radical by the hydrogen abstraction from solvent or elsewhere. Tetraphenylmethane is a cage product of a trityl radical with a phenyl radical. Other products, 3,3,3-triphenylpropionitrile (**3**) and [4-(diphenylmethyl)phenyl]acetonitrile (**4**), are adducts of trityl radicals and cyanomethyl radicals which are generated by hydrogen abstraction from acetonitrile by a phenyl radical. The formation of **2** might be explained by an intramolecular

Table 1. Product Yield of Decomposition of **PAT**[a)]

	Yield (%)[b)]					
	TPP$^+$ sens.		**DCA** sens.	Direct		Thermolysis
	> 405 nm	366 nm	> 405 nm	> 405 nm	313 nm	60 °C
PhH	90	93	87	100	95	100
2	35	5	6	3	4	1
Ph_3CH	0	13	12	9	11	6
Ph_4C	3	7	2	3	1	2
3	15	14	25	40	35	35
4	0	4	24	36	23	22

a) See Experimental Section for reaction conditions. b) Conversions are 100% in all experiments, and yields were determined by GC.



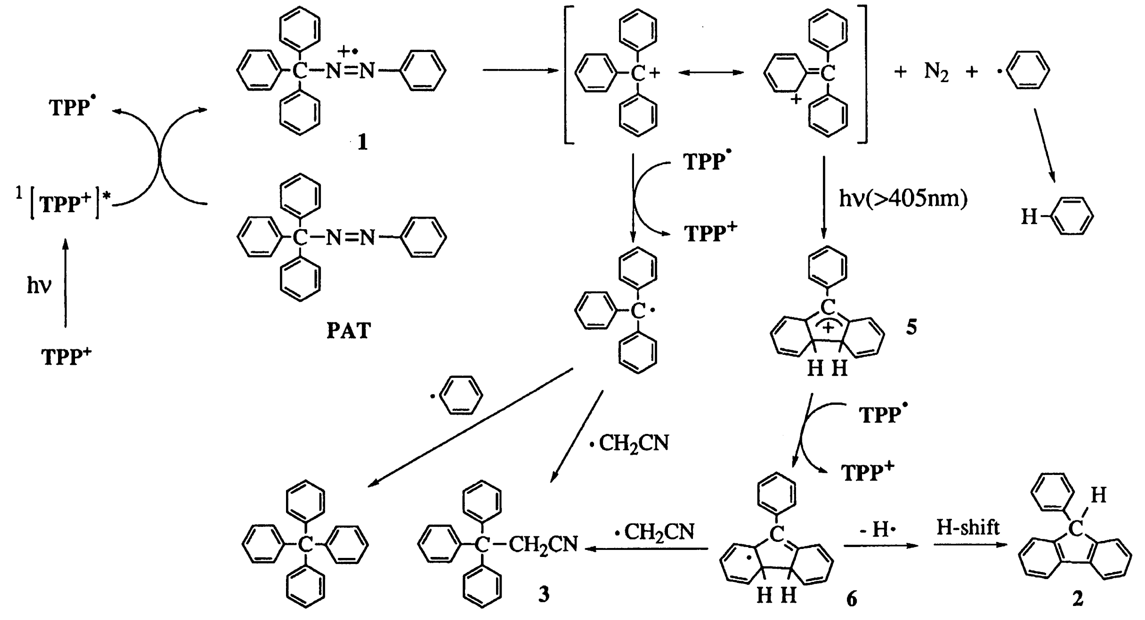
Scheme 1.

photocyclization of a trityl radical,[13] though it is not a major pathway because the yield of **2** is not high, only a few percent. To confirm this, **PAT** was directly photolyzed at 313 nm light which could be absorbed by a trityl radical;[14,15] however, the product yields were not changed and the yields was almost the same as that by >405 nm irradiation, as shown in Table 1. From these results it could not be confirmed that **2** was produced by the irradiation of a trityl radical.

In order to compare the product distribution of **DCA** sensitized photolysis and that of the typical radical decomposition of **PAT**, thermolysis and direct photolysis at >405 nm light were examined. Product distributions of both radical reactions are also shown in Table 1. Benzene is obtained quantitatively in both reactions, and surprisingly, the product distributions of both reactions are quite similar to that of **DCA** sensitization reaction. These results mean that the products were not obtained from the radical cations but from the radicals, even in the case of **DCA**-sensitization. The fact that we could not obtain the radical cation derived products, *N*-(triphenylmethyl)acetamide and **2**, indicates that the generated cation had a short lifetime. It is apparent the back electron transfer occurs between a trityl cation and a **DCA** radical anion, and then the trityl radical is generated. The generated trityl radicals could behave to afford products as shown in Scheme 1.

On the other hand, the result of $\mathbf{TPP^+}$ sensitization at >405 nm light is quite interesting. The mass balance is lower than those of other decomposition reactions similar to other $\mathbf{TPP^+}$ sensitized reactions,[2c,16] and complex products may be obtained by the reaction between the generated radical intermediates and the generated 2,4,6-triphenylpyranyl radical (**TPP•**).[17] The product distribution is drastically changed from those of other reactions: thermolysis, direct photolysis, and even **DCA**-sensitized photolysis. Compound **2** is one of the major products which are derived from trityl moieties. The yield of **3** is lower than those of other reactions, and triphenylmethane and **4** are not obtained. The reaction mechanism is shown in Scheme 2. This difference of the product yields can be explained from the characteristic property of the sensitizer, $\mathbf{TPP^+}$. The electron accepted $\mathbf{TPP^+}$, **TPP•**, is moderately stable[18] and the rate of back electron transfer to the trityl cation is slow, and the lifetime of the trityl cation is longer than that in the case of **DCA** sensitization. The difference of the rates of back electron transfer can be understood from the difference of ΔG values of back electron transfer, ΔG_{bet}, too. The ΔG_{bet} values are estimated by the following equation: $\Delta G_{\mathrm{bet}}=-(E_{\mathrm{ox}}-E_{\mathrm{red}}-e_0^2/\varepsilon_{\mathrm{a}})$ ($e_0^2/\varepsilon_{\mathrm{a}}=0.7$ kcal mol^{-1} in acetonitrile).[2f] The oxidation potential of trityl radical is -0.08 V vs. SCE[19] and the reduction potentials of electron accepted sensitizers, **DCA** radical anion and **TPP•**, are -0.89 and -0.29 V vs. SCE, respectively.[10] From these values, the estimated ΔG_{bet} values are -17.9 and -4.1 kcal mol^{-1} in the cases for **DCA** radical anion and **TPP•**, respectively. The rate of the back electron transfer could be fast in the case of **DCA** radical anion, but the negative small value may reflect the slow rate of the back electron transfer in the case for **TPP•**. The slow rate of the back electron transfer reflects the product distribution. Compounds **3** and **4** are adducts between cyanomethyl radicals, which are generated by the hydrogen abstraction from acetonitrile by phenyl radicals, and trityl radicals. Their yields are small in $\mathbf{TPP^+}$ sensitization reactions. These results can be explained if the cyanomethyl radical can not survive for the slow generation of the trityl radical by the slow back electron transfer.

The difference of the rate of the back electron transfer is confirmed by the experiments of laser flash photolysis. Figure 1 shows the transient absorption spectra of **PAT** observed upon the excitation of **DCA** or $\mathbf{TPP^+}$ as a sensitizer with a 355 nm laser light in argon-purged acetonitrile. In the presence of **DCA**, only a weak absorption which must be a tail



Scheme 2.

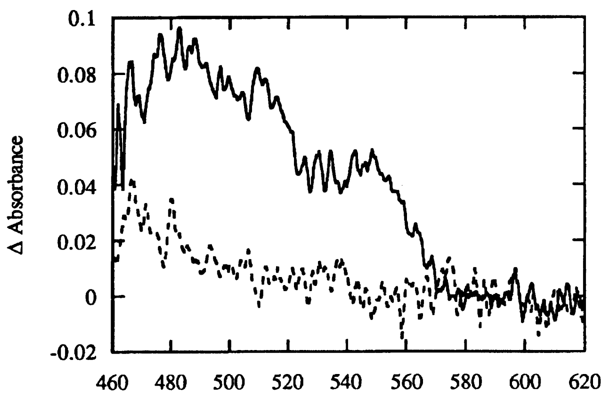


Fig. 1. Transient absorption spectra of **PAT** in the presence of $\mathbf{TPP}^+$ (solid line) or **DCA** (dashed line) 200 ns after laser pulse in argon purged acetonitrile at room temperature.

of a trityl radical absorption band is observed. It is reported that an absorption maximum of a trityl radical is around 335 nm.[14,15] In the region of wavelength shorter than 460 nm, the absorption of ground state **DCA** is too strong to observe the absorption of a trityl radical under these experimental conditions. The absorption of **DCA** radical anion which appeared around 500—700 nm[20] could not be observed. These results mean a trityl cation accepts an electron from a **DCA** radical anion by the back electron transfer to generated a trityl radical, and this process must be faster than twenty or thirty nano-seconds (instrumental resolution). From these results, we can explain the mechanism from the product distribution of **DCA** sensitized reaction. The products are derived from trityl radicals which are produced by the back electron transfer and therefore, the distribution is the same as those of the direct photolysis and the thermolysis.

In the case of $\mathbf{TPP}^+$, a strong transient absorption was observed around 480 nm. $\mathbf{TPP}^+$ has an absorption which is shorter than 460 nm and at this region no transient absorption can be observed at this experimental condition. However, we assigned the transient absorption to a trityl cation which is reported to have an absorption around 420—440 nm and a weak band around 480 nm.[15,21] Furthermore, the absorption assigned to **TPP•** is observed around 550 nm[18] with a lifetime in 10 μs. This indicates the back electron transfer to the trityl cation is slow. These results support our assumption that the rate of back electron transfer between a trityl cation and a **TPP•** is slow and the trityl cation could survive for proceeding to the cationic reaction. The difference between the product distribution of the $\mathbf{TPP}^+$ sensitization reaction and those of other types of reaction conditions is contained in the above explanation.

The photocyclization reaction of a trityl cation is postulated for the formation of **2**, as shown in Scheme 2.[22] In the $\mathbf{TPP}^+$ sensitization reaction, when the irradiation light wavelength was > 405 nm the generated trityl cation could absorb the light and produce **2**. In order to confirm this postulation, $\mathbf{TPP}^+$ sensitized photolysis of **PAT** at 366 nm light at which trityl cation was transparent was performed. The products yields are listed in Table 1; compound **2** is obtained in only 5% yield. This result indicates that the photoreaction of trityl cation produces **2**. In $\mathbf{TPP}^+$ sensitized reaction at 366 nm, the generated trityl cation can not absorb the light and survives. But finally, it accepts an electron from **TPP•**, though the rate of its back electron transfer is slow. Then, trityl radical derived products like triphenylmethane, **3**, and **4**, are obtained. In $\mathbf{TPP}^+$ sensitized reaction at > 405 nm light, **3** is obtained in 15% yield. However, we can not consider the generation of **3** via recombination of the trityl radical and the cyanomethyl radical as described for the $\mathbf{TPP}^+$ sensitization at 366 nm. If **3** is derived from a trityl radical in these conditions, the absence of triphenylmethane and **4** can not be explained. Therefore, we think **3** is also a product from the trityl cation as well as **2** in **TPP**$^+$ sensitized reaction at 405 nm irradiation. As shown in Scheme 2, **3** is produced through the ring opening initiated by the addition of cyanomethyl radical to **6**; an intermediate formed by the back electron transfer from **TPP**· to the photocyclized cation (**5**). It is reported that acetonitrile reacts with cations as a nucleophile to give a Ritter-adduct.[16,23] However, we could not detect *N*-(triphenylmethyl)acetamide($Ph_3CNHCOCH_3$) in this case, and a similar result is reported in ground state charge transfer experiments.[1]

The decomposition mechanisms of **PAT** are clarified. It is found that the nature of the sensitizer in the geminal radical-ion pair controls the rate of back electron transfer, the fate of the generated intermediate, and then the product distribution in the PET reaction.

References

1) H. J. Shine, D. H. Bae, A. K. M. M. Hoque, A. Kajstura, W. K. Lee, R. W. Shaw, M. Soroka, P. S. Engel, and D. E. Keys, *Phosphorus Sulfur*, **23**, 111 (1985).

2) a) P. S. Engel, D. E. Keys, and A. Kitamura, *J. Am. Chem. Soc.*, **107**, 4964 (1985); b) H. Ikeda, T. Minegishi, and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, **1994**, 297; c) W. Adam, C. Sahin, J. Sendelbach, H. Walter, G.-F. Chen, and F. Williams, *J. Am. Chem. Soc.*, **116**, 2576 (1994); d) T. A. Zona and J. L. Goodman, *J. Am. Chem. Soc.*, **117**, 5879 (1995); e) T. Karatsu, H. Itoh, T. Kikunaga, Y. Ebashi, H. Hotta, and A. Kitamura, *J. Org. Chem.*, **60**, 8270 (1995); f) H. Ikeda, T. Minegishi, Y. Takahashi, and T. Miyashi, *Tetrahedron Lett.*, **39**, 4377 (1996), and references cited therein.

3) a) A. Kitamura, H. Sakuragi, M. Yoshida, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **53**, 1393 (1980); b) H. Misawa, A. Kitamura, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **57**, 1167 (1984).

4) R. Akaba, Y. Niimura, T. Fukushima, Y. Kawai, T. Tajima, T. Kuragami, A. Negishi, M. Kamata, H. Sakuragi, and K. Tokumaru, *J. Am. Chem. Soc.*, **114**, 4460 (1992).

5) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953).

6) J. A. Sanguigni and R. Levine, *J. Med. Chem.*, **7**, 573 (1964).

7) L. Hellerman and R. L. Garner, *J. Am. Chem. Soc.*, **68**, 820 (1946).

8) J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 6083 (1980).

9) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), p. 99.

10) M. Chanon and L. Eberson, in "Photoinduced Electron Transfer," ed by M. A. Fox and M. Chanon, Elsevier, New York (1988), Part A, p. 470.

11) D. Rehm and A. Weller, *Ber. Busenges. Phys. Chem.*, **73**, 834 (1969); *Isr. J. Chem.*, **8**, 259 (1970).

12) G. J. Kavarnos, in "Photoinduced Electron Transfer 1, Topics in Current Chemistry 156," Springer-Verlag, Berlin (1990), p. 31.

13) a) M. A. Fox, E. Gaillard, and C.-C. Chen, *J. Am. Chem. Soc.*, **109**, 7088 (1987); b) J. A. Schmidt and E. F. Hilinski, *J. Am. Chem. Soc.*, **110**, 4036 (1988).

14) A. Bromberg, K. H. Schmidt, and D. Meisel, *J. Am. Chem. Soc.*, **107**, 83 (1985).

15) J. L. Faria and S. Steenken, *J. Am. Chem. Soc.*, **112**, 1277 (1990).

16) T. Karatsu, Y. Ichino, A. Kitamura, W. H. Owens, and P. S. Engel, *J. Chem. Res. (S)*, **1995**, 440; (*M*), **1995**, 2534.

17) S. Kyushin, Y. Nakadaira, and M. Ohashi, *Chem. Lett.*, **1990**, 2191.

18) T. Karatsu, H. Kobayashi, E. Shinkai, and A. Kitamura, *Chem. Lett.*, **1992**, 2131.

19) a) R. Breslow, W. Bahary, and W. Reinmmuth, *J. Am. Chem. Soc.*, **83**, 1763 (1961); b) R. Breslow and K. Balasubramanion, *J. Am. Chem. Soc.*, **91**, 5182 (1969).

20) T. Shida, in "Electronic Absorption Spectra of Radical Ions," Physical Science Data 34, Elsevier, New York (1988), p. 246.

21) L. E. Manring and K. S. Peters, *J. Phys. Chem.*, **88**, 3516 (1984).

22) E. D. Owen and D. M. Allen, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 95.

23) P. S. Engel, W.-K. Lee, G. E. Marschke, and H. J. Shine, *J. Org. Chem.*, **52**, 2813 (1987).