

Photoinduced Electron Transfer Reactions of 3*H*-Pyrazole Derivatives. Formation of Solvent Adduct by Specific Sensitizer

Takashi Karatsu,* Nobuo Shiochi, Takumi Aono, Nobukazu Miyagawa, and Akihide Kitamura*

Department of Materials Technology, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522

(Received October 17, 2002)

3*H*-pyrazoles were photolyzed in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP⁺) or 9,10-dicyanoanthracene (DCA) as a sensitizer. The obtained products were different depending on the sensitizers employed. The cyclopropene derivatives were produced in the cases of the DCA and TPP⁺ sensitizations and a solvent adduct was obtained for the TPP⁺ sensitization reaction. The difference in products is explained by the rates of the back electron transfer from the electron accepted sensitizers to the radical cation intermediates. In the DCA sensitization, the absorption band of the diazoalkene was observed but in the TPP⁺ sensitization it was not observed. From these results, it is apparent that the back electron transfer rates of the DCA sensitization reactions are faster than those of the TPP⁺ sensitization reactions.

Many photoinduced electron transfer (PET) reactions of cyclic azoalkanes have been studied, however, in most cases, the photodenitrogenation products were obtained in the PET reaction similar to the direct photolysis.¹ Few characteristic products are hardly obtained by the PET reaction. In the PET reaction of a five-membered cyclic azoalkane, pyrazoline, the rearranged product was produced with the cyclopropane which is the only product in the thermolysis and in the direct photolysis.² This difference in products was explained by the stability of the radical cation intermediates. In our previous short communication, we reported the PET reaction of 3*H*-pyrazoles which have an unsaturated carbon–carbon double bond with an azo chromophore in its five-membered skeleton.³ The direct photolysis of the 3*H*-pyrazoles had been already reported and the corresponding cyclopropene derivatives were produced after the observation of the diazoalkene precursors.⁴ In the paper, we showed the interesting result that the use of different sensitizers induced different products. In the 9,10-dicyanoanthracene (DCA) sensitization, only the cyclopropene was produced, but in the 2,4,6-triphenylpyrylium tetrafluoroborate (TPP⁺) sensitization, an adduct with the solvent, acetonitrile, was produced with the cyclopropene. In the PET reactions, the formations of solvent adducts have been reported by several groups.⁵ Such formation means that the lifetime of the intermediate radical cation is long enough to react with the solvent.

In this paper, we show the total reaction mechanism of the 3*H*-pyrazoles which is confirmed from some experiments involving both the DCA and the TPP⁺ sensitization.

Results and Discussion

In order to investigate the interaction between the excited singlet sensitizers and 3*H*-pyrazoles, fluorescence quenching experiments were performed. The obtained quenching rate constants (k_q) are summarized in Table 1. The fluorescence of TPP⁺ was quenched at the nearly diffusion rate constants

Table 1. Redox Potentials of 3*H*-Pyrazoles, Their Quenching Rate Constants (k_q) by TPP⁺ and DCA, and Their Free Energy Change (ΔG) Relationship

Compound	E_{ox}/V E_{red}/V		$\Delta G/\text{kcal mol}^{-1}$		$k_q/\text{L mol}^{-1} \text{s}^{-1}$	
	vs SCE		TPP ⁺	DCA	TPP ⁺	DCA
1	2.05	−1.45	−11.8	+1.2	1.6×10^{10}	6.4×10^9
2	2.05	−1.59	−11.8	+1.2	1.1×10^{10}	1.3×10^9
3	2.02	—	−12.5	+0.5	1.7×10^{10}	1.5×10^9

by 3*H*-pyrazoles, but the quenching rate constants of DCA by the 3*H*-pyrazoles were five to ten times lower than those of TPP⁺. The differences in the free energy (ΔG) calculated from the measured oxidation potentials of **1** and **2**, using the Rehm–Weller equation,⁶ are shown in Table 1. The difference in k_q s can be explained from these values. For TPP⁺, ΔG values are exergonic and an electron certainly transfers from a molecule of the 3*H*-pyrazoles to the excited singlet TPP⁺ molecule at the diffusion-controlled rate constants. On the other hand, for DCA, the ΔG values are slightly endergonic and the k_q values must reflect these relations. In Table 1, the reduction potentials of **1** and **2** are also listed. These values are not used to calculate ΔG , but they are useful for understanding the redox correlation between the sensitizers and 3*H*-pyrazoles. Furthermore, the oxidation potential of **3** and the quenching rate constants by **3** are listed in Table 1.

The electron transfer between the sensitizer and 3*H*-pyrazole is also supported by the observation of a pyranil radical (TPP•) during the laser flash photolysis experiment. The transient absorption spectrum was observed at around 550 nm after the laser pulse and it lived for ca. 50 μs ; this is assigned to the pyranil radical absorption.^{7,8} The observation of the pyranil radical means that an electron transferred from a ground state 3*H*-pyrazole to an excited singlet state TPP⁺. However, the electron donated species, the 3*H*-pyrazole radical cation or its derived species, was not observed as the transient absorp-

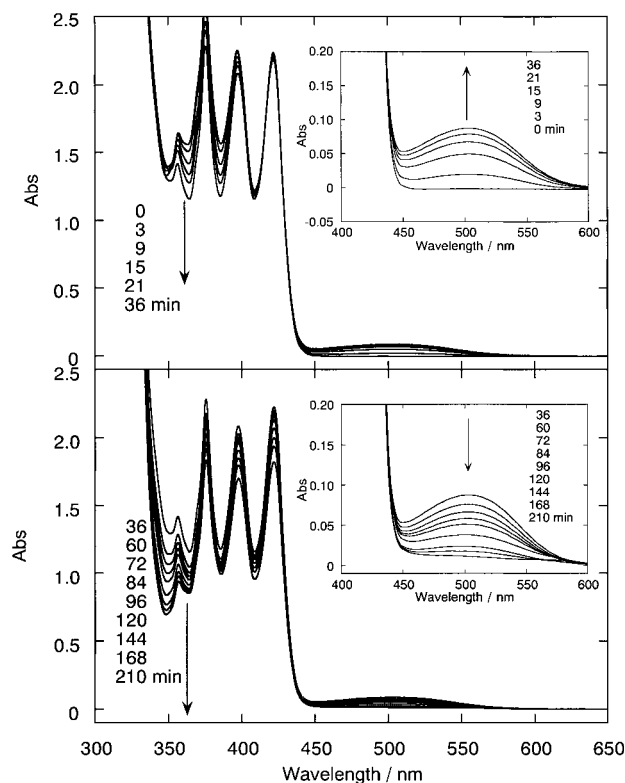


Fig. 1. Absorption spectra of **1** (4.4×10^{-3} mol dm $^{-3}$) in the presence of DCA (4.2×10^{-4} mol dm $^{-3}$) in acetonitrile for various irradiation times. Inset: Expansion of the wavelength between 400 and 640 nm.

tions probably owing to an overlap with the absorption of TPP $^{+}$.

In the DCA sensitizations, **1** and **2** were efficiently decomposed and produced the same compound, **3**. The yields were 45% and 85%, respectively. During the direct photolyses of **1** and **2**, **3** was obtained and the presence of precursors, diazoalkene derivatives **5** and **6**, were confirmed from the UV absorption spectra which had maximum wavelengths of 420 nm and 510 nm, respectively.⁴ These diazoalkene compounds were generated by the radical cleavages of the carbon–nitrogen bonds of **1** and **2**. During the TPP $^{+}$ sensitization reactions, we did not observe the diazoalkene precursors, but surprisingly we observed the generation of **6** for the DCA sensitization of **2**. The absorption band, which had a maximum at 510 nm, was gradually increased and then decreased by the irradiation as shown in Fig. 1. We believe **5** must be also generated during the DCA sensitization of **1**, although it could not be observed in the absorption spectra due to the overlapping with the absorption band of DCA. The mechanism of these reactions looks to be the same as the direct photolysis and the thermolysis, which means that the back electron transfer (BET), from the DCA anion radical to the C–N bond cleaved cation radical, **8**, **9** or **10**, occurred under the contact ion pairs.⁷ The laser flash photolysis experiments supported this estimation. The transient absorption spectrum of the radical anion of DCA⁹ was observed after the laser pulse in the presence of DCA and biphenyl, and its lifetime was 8 μ s. However, in the presence of DCA and **1**, the lifetime of the anion radical of DCA

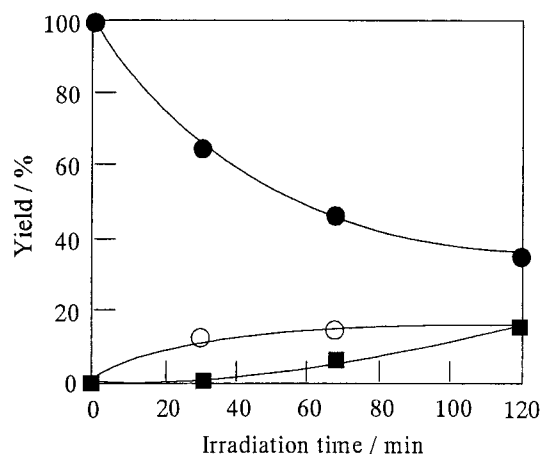
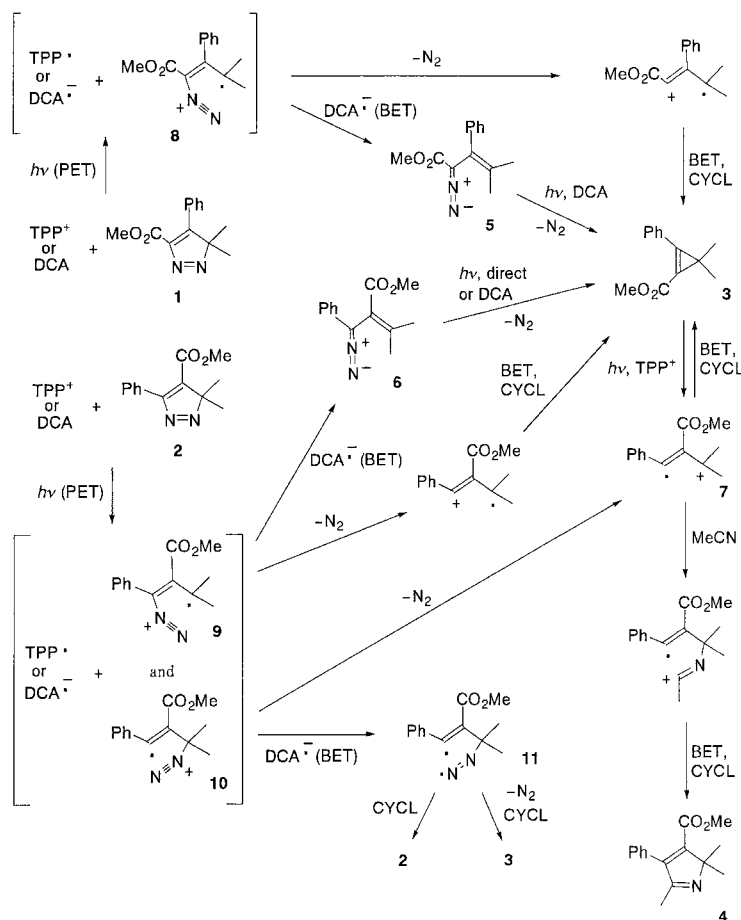


Fig. 2. Decomposition of **1** and formation of products in the presence of TPP $^{+}$ by the irradiation of 405-nm light. **1** (●); **3** (○); **4** (■).

was < 50 ns. This very short lifetime must be caused by the fast BET under the contact ion pairs. On the other hand, for TPP $^{+}$, the BET does not efficiently occur because of producing the solvent separated pairs more rapidly.¹⁰ The formation of **3** is induced by the decomposition of **5** and **6**. These reaction mechanisms are not certain, but **5** may be decomposed by DCA sensitization because **5** cannot directly absorb the light owing to the overlap with the absorption of DCA. On the other hand, the sensitized and/or direct photolysis of **6** is presumed to occur by the absorption because the absorption band of **6** is isolated from that of DCA.

During the TPP $^{+}$ sensitization reactions, both **1** and **2** afforded the same products, **3** and **4**. The characteristic compound **4** would be an adduct of the 1,3-radical cation, **7**, with the solvent, acetonitrile. The production of the same compound from the different reactions means the presence of the same intermediate or precursor. In order to resolve the reaction mechanism, we examined the irradiation time correlations of these product yields. In the TPP $^{+}$ sensitization reaction of **1**, during the primary stage, the cyclopropene **3** was generated according to the consumption of the starting material. After 1 h, the yield of **3** reached a plateau, then the yield of **4** gradually increased after a short induction time (Fig. 2). For the reaction of **2**, **4** was generated rather than **3** at the initial stage (Fig. 3). The controlled experiments showed that the TPP $^{+}$ sensitization reaction of **3** gave **4**, however, only the consumption of **4** and no formation of **3** were observed by the TPP $^{+}$ sensitization of **4**.

From the results of these experiments, we confirmed the total reaction mechanism of the DCA and TPP $^{+}$ sensitization of the 3H-pyrazoles, **1** and **2**, as shown in Scheme 1. During the DCA sensitization reaction of **1**, the electron transfer occurred to generate the radical cation of **1** and produce the radical cation **8** by the carbon–nitrogen bond cleavage. Then, the formation of the diazoalkene **5** is observed by the fast BET process between **8** and the DCA radical anion, and next nitrogen **3** is eliminated. No further reaction occurred in the case of DCA. On the other hand, for the TPP $^{+}$ sensitization reaction of **1**, the electron transfer occurred to generate the radical cation of **1**, and produce the radical cation **8** by the carbon–nitro-



Scheme 1.

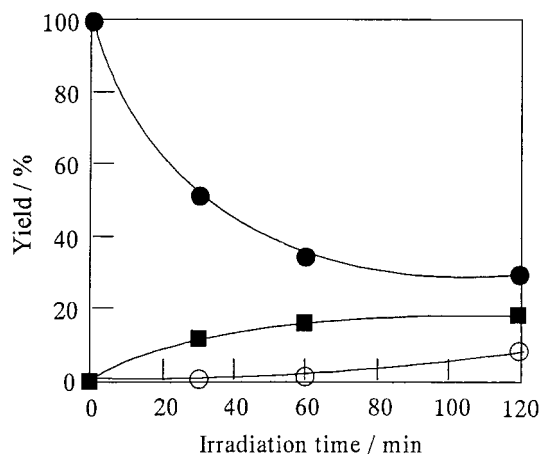


Fig. 3. Decomposition of **2** and formation of products in the presence of TPP⁺ by the irradiation of 405-nm light. **2** (—●—); **3** (—○—); **4** (—■—).

gen bond cleavage. Then, **8** eliminates nitrogen and the cyclopropene **3** is produced by the BET and the recyclization (CYCL) of the generated 1,3-radical cation. Furthermore, in the presence of TPP⁺, the carbon–carbon bond of **3** is cleaved by the PET reaction to form the isomeric 1,3-radical cation **7**, then, acetonitrile, which is a weak nucleophile, adds to **7**, resulting in the formation of 2*H*-pyrrole **4**.

The sensitized reaction mechanism of **2** is more complex

than that of **1**. There are two reaction paths. One is the path via the intermediate **9** and the other is the path via the intermediate **10**. The difference of the cleaved carbon–nitrogen bonds of the radical cation of **2** induces two kinds of radical cations, **9** and **10**. After the generation of **9**, the reaction proceeds similarly to the case of **8**. In the DCA sensitization reaction, the generation of **6** is observed and the product is the cyclopropene **3**, and in the TPP⁺ sensitization reaction the cyclopropene **3** and 2*H*-pyrrole **4** are obtained. The fate of **10** is different from those of **8** and **9**. In the DCA sensitization reaction, the biradical **11** is produced by the BET between **10** and the DCA radical anion, and the cyclopropene **3** and the starting material, 3*H*-pyrazole **2** would be produced. In the TPP⁺ sensitization reaction, the radical cation **10** eliminates nitrogen and the 1,3-radical cation **7** is directly produced, and then the cyclopropene **3** and 2*H*-pyrrole **4** are obtained.

All the results can be clearly explained by the reaction mechanism of Scheme 1 except for one problem, why the mechanism was different in the reactions of **1** and **2**. In Scheme 1, it is shown that the decomposition of **1** proceeds through the intermediate of the bond cleaved radical cation, **8**. On the other hand, during the reaction of **2**, there are two patterns of carbon–nitrogen bond cleavage and radical cations **9** and **10** are generated. This difference in the bond cleavage pattern is supported by the AM1 calculation. In the model calculations for the cationic reactions in vacuum, therefore, the activation energies seem to be too high for efficient

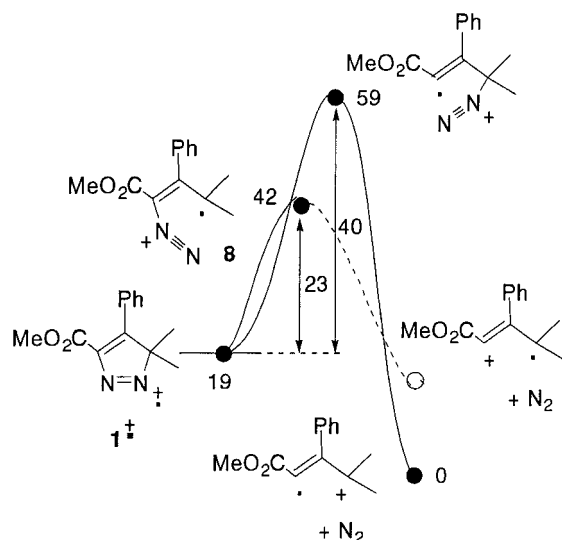


Fig. 4. Potential energy diagrams of radical cations derived from **1** by AM1 calculation. The values of the closed circles are calculated, but the value of the open circle was not obtained, because another 1,3-radical cation is more stable and the result of the calculation corresponds to the more stable 1,3-radical cation with the eliminated nitrogen.

reactions. These values for cationic reactions must take much smaller values in polar solvents. The bond cleavage of the radical cation of **1** is endothermic and the activation energy to generate the radical cation of **8** from **1** is 23 kcal mol⁻¹, but that of the opposite side C–N bond cleavage requires about 40 kcal mol⁻¹ (Fig. 4). This is the reason why the reaction proceeds through the intermediate **8**, and then the 1,3-radical cation is generated by the elimination of nitrogen. For the reaction of **2**, the activation energies to generate the radical cation **9** or **10** are quite similar, 26 and 27 kcal mol⁻¹, respectively (Fig. 5). Therefore, the reaction proceeds through two paths, one is the path via the radical cation **9** and the other is the path via the radical cation **10**.

More important information from the calculation is obtained for the propenyl and cyclopropenyl radical cations. If the cyclopropenyl radical cation of **3** is generated by the PET reaction of **3**, the C–C (benzyl carbon) bond is easier to cleave than the other C–C bonds (Fig. 6). This lower activation energy leads to the formation of the acetonitrile adduct **4**.

We are interested in the PET reactions of cyclic azo compounds, and especially the behavior of the generated radical cations. In this case we found a fairly stable 1,3-radical cation which can react with the solvent, acetonitrile. We are now studying more stable radical cations which are generated from cyclic azo compounds.

Experimental

Materials. The sensitizers were purified by recrystallization, and dehydrated acetonitrile (Kanto Chemical Co.) was used. Methyl 3,3-dimethyl-4-phenyl-3H-pyrazole-5-carboxylate (**1**) and methyl 3,3-dimethyl-5-phenyl-3H-pyrazole-4-carboxylate (**2**) were prepared by the cycloaddition of 2-diazopropane to methyl phenylpropionate.⁴ Methyl 3,3-dimethyl-1-phenylcyclopropene-2-carboxylate (**3**)⁴ was isolated from the pyrolyzed sample of **1**.

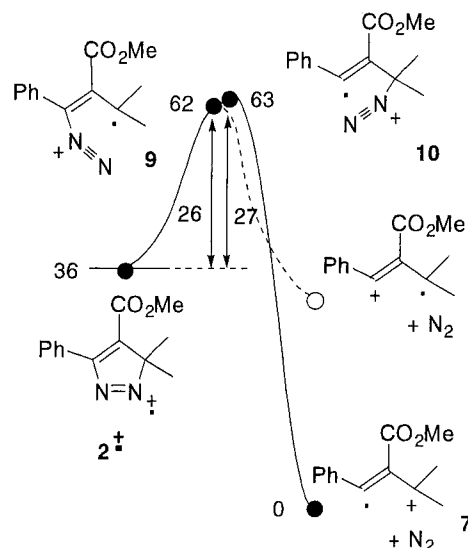


Fig. 5. Potential energy diagrams of radical cations derived from **2** by AM1 calculation. The values of the closed circles are calculated, but the value of the open circle was not obtained, because another 1,3-radical cation is more stable and the result of the calculation corresponds to the more stable 1,3-radical cation with the eliminated nitrogen.

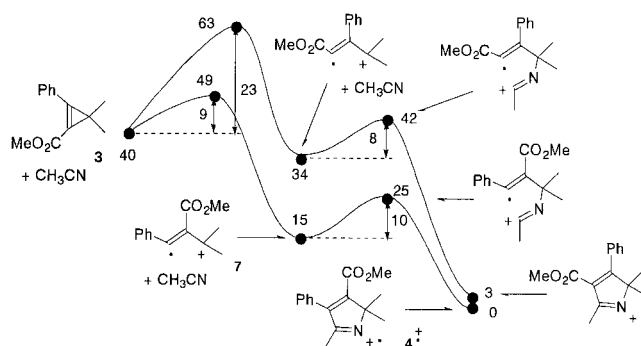


Fig. 6. Potential energy diagrams of radical cations derived from **3** by AM1 calculation.

Synthesis of Methyl 2,2-Dimethyl-4-phenyl-2H-pyrole-3-carboxylate (4**).** A solution of 1 mmol of **1** in 25 mL of acetonitrile with 30 mg of TPP⁺ was distributed into 6 irradiation tubes, and then degassed by freeze-thaw cycles. The degassed samples were irradiated at 405 nm for 10 h, and then the samples were collected and concentrated. After removal of TPP⁺ through a short column chromatography (AcOEt), the residue was concentrated and purified by preparative TLC (CHCl₃/AcOEt). A colorless oil was obtained in 15% yield. ¹H NMR (270 MHz, CDCl₃) δ 7.42–7.38 (m, 2H, Ar), 7.25–7.19 (m, 3H, Ar), 3.61 (s, 3H, CO₂Me), 2.12 (s, 3H, MeC=N), 1.45 (s, 6H, Me). NOE was observed between the aromatic proton and the methyl proton derived from the MeCN unit. HRMS (EI) Calcd for C₁₅H₁₇NO₂ 243.1259, found 243.1251.

Fluorescence Quenching Experiments. The electron transfer rate constant was determined by the change in the fluorescence intensity of DCA (1.9 × 10⁻⁴ mol dm⁻³) or TPP⁺ (5.2 × 10⁻⁴ mol dm⁻³) during the addition of various concentrations of the 3H-pyrazoles (0–1 × 10⁻² mol dm⁻³) in acetonitrile under degassed condition.

Redox Potential Measurements. The oxidation and the reduction potentials of the 3*H*-pyrazoles were measured by cyclic voltammetry (BAS CV-1B) at a platinum electrode in argon-saturated dry acetonitrile with 0.1 mol dm⁻¹ tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The scan speed was 200 mV s⁻¹ and the reference electrode was a SCE. The obtained peaks were irreversible, and the potentials were determined from the half-peak potentials.

Transient Absorption Measurements. 2.3 × 10⁻⁵ mol dm⁻³ of TPP⁺ and 2.2 × 10⁻³ mol dm⁻³ of **1**, 2.7 × 10⁻³ mol dm⁻³ of DCA and 2.0 × 10⁻¹ mol dm⁻³ of biphenyl, 2.7 × 10⁻³ mol dm⁻³ of DCA and 1.7 × 10⁻³ mol dm⁻³ of **1**, respectively, are dissolved in acetonitrile; argon gas was bubbled for 20 min and the transient absorptions were measured. They were measured by 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 270 M monochromometer (resolution: 0.3 nm/channel).¹¹

Reactions. Direct Photolyses of 1 and 2: 2.9 × 10⁻³ mol dm⁻³ of **1** or **2** was dissolved in acetonitrile. After being degassed by the freeze-thaw in a tube with a UV cell, the sample was irradiated by 366-nm light using a 1-kW high pressure mercury lamp through a glass filter. The reactions were pursued by UV and GC analysis.

DCA Sensitized Photolyses of 1 and 2: **1** or **2** and DCA were dissolved in acetonitrile to make a solution having a concentration of 4.4 × 10⁻³ mol dm⁻³ of **1** or **2** and 4.2 × 10⁻⁴ mol dm⁻³ of DCA which was nearly saturated. After being degassed by the freeze-thaw, the sample was irradiated by 405-nm light using a 1-kW high pressure mercury lamp through a CuSO₄ + NaNO₂ + aqueous ammonia solution filter.¹² The reactions were monitored by GC analysis.

TPP⁺ Sensitized Photolyses of 1 and 2: **1** or **2** and TPP⁺ were dissolved in acetonitrile to make a solution having a concentration of 5.7 × 10⁻³ mol dm⁻³ of **1** or **2** and 1.4 × 10⁻³ mol dm⁻³ of TPP⁺. After being degassed by the freeze-thaw, the sample was irradiated by 405-nm light using a 1-kW high pressure mercury lamp through the solution filter. The reaction was monitored by GC analysis.

A part of this work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology and the Futaba Denshi Foundation.

References

- 1 a) W. Adam, U. Denninger, R. Fenzel, F. Kita, H. Platsch, H. Walter, and G. Zang, *J. Am. Chem. Soc.*, **114**, 5027 (1992). b) W. Adam and J. Sendelbach, *J. Org. Chem.*, **58**, 5316 (1993).
- 2 a) H. Ikeda, T. Minegishi, and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, **1994**, 297. d) H. Ikeda, T. Minegishi, Y. Takahashi, and T. Miyashi, *Tetrahedron Lett.*, **37**, 4377 (1996).
- 3 a) T. Karatsu, H. Hotta, and A. Kitamura, *J. Chem. Soc., Chem. Commun.*, **1991**, 1451. b) T. Karatsu, H. Itoh, T. Kikunaga, Y. Ebashi, H. Hotta, and A. Kitamura, *J. Org. Chem.*, **60**, 8270 (1995).
- 4 N. Miyagawa, T. Karatsu, and A. Kitamura, *Chem. Lett.*, **1997**, 1005.
- 5 M. Frank-Neumann and C. Buchecker, *Tetrahedron Lett.*, **1**, 15 (1969).
- 6 a) T. A. Zona and J. L. Goodman, *Tetrahedron Lett.*, **33**, 6093 (1992). b) K. Mizuno, K. Nire, H. Sugita, and Y. Otsuji, *Tetrahedron Lett.*, **34**, 6563 (1993). c) H. J. P. deLijser and D. R. Arnold, *J. Org. Chem.*, **62**, 8432 (1997).
- 7 a) D. Rehm and A. Weller, *Ber. Bunsen-Ges. Phys. Chem.*, **73**, 834 (1969). b) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).
- 8 T. Karatsu, H. Kobayashi, E. Shinkai, and A. Kitamura, *Chem. Lett.*, **1992**, 2131.
- 9 N. Miyagawa, T. Karatsu, Y. Futami, T. Kunihiro, A. Kiyata, and A. Kitamura, *Bull. Chem. Soc. Jpn.*, **69**, 3325 (1996).
- 10 I. R. Gould, D. Ege, J. E. Moser, and S. Farid, *J. Am. Chem. Soc.*, **112**, 4290 (1990).
- 11 T. Karatsu, K. Kanayama, M. Takahashi, N. Ishigoka, K. Fukui, and A. Kitamura, *Heteroatom Chem.*, **12**, 269 (2001).
- 12 T. Karatsu, H. Itoh, N. Yoshikawa, A. Kitamura, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **72**, 1839 (1999).
- 13 J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 6083 (1980).