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Photochemical C-P Bond Cleavage of Nitrobenzylphosphonate Ions

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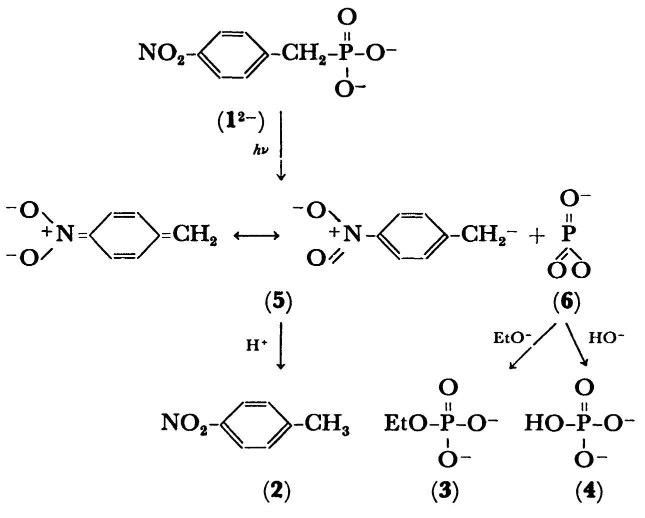
Upon UV-irradiation, the C–P bond of *p*-nitrobenzylphosphonate ions cleaved with a quantum yield of about 0.7 in an aqueous alcohol solution to give 1,2-bis(4-nitrophenyl)ethane, *p*-nitrotoluene, orthophosphate, and alkyl dihydrogenphosphate. Whereas in an aqueous solution 1,2-bis(4-nitrophenyl)ethane was produced as a main product, in an alcohol solution only *p*-nitrotoluene was produced. This photolysis may proceed via intramolecular electron transfer from PO_3^{2-} group to nitro aromatic moiety to form an excited state, which undergoes C–P bond cleavage to give *p*-nitrobenzyl anion and monomeric metaphosphate anion as intermediates. The C–P bond cleavage of *p*-nitrobenzylphosphonate ion occurred more readily than those of *o*- and *m*-nitrobenzylphosphonate ions.

The chemical and thermal stability of C–P bond in free alkylphosphonic acid is well-known and chemical reactions involving C–P bond cleavage are not common.1) The thermal decomposition of 2-haloalkylphosphonic acid is one of a few examples.2) The C–P bond of this acid is easily cleaved into the fragments of 1-alkene, halide, and orthophosphate in a basic aqueous solution. The photochemical C–P bond cleavage of free phosphonic acid has not been reported before our previous letter.3) Upon UV-irradiation of a basic 80% ethanol solution of *p*-nitrobenzylphosphonic acid (**1**), the formations of *p*-nitrotoluene (**2**), and salts of ethyl dihydrogenphosphate (**3**) and orthophosphoric acid (**4**) were observed.3) We have suggested that this process involves an unimolecular C–P bond cleavage to give *p*-nitrobenzyl anion (**5**) and monomeric metaphosphate anion (**6**) as intermediates (Scheme 1). When anhydrous alcohol solutions of **1** containing 2 molar equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were irradiated, alkyl dihydrogenphosphates were obtained in almost quantitative yields.4)

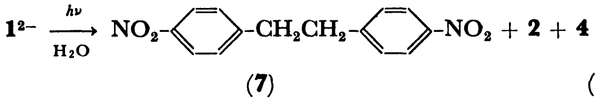
In the present paper, we will report the more detail investigation of photolysis of nitrobenzylphosphonic acids.



Scheme 1.

Results and Discussion

Photolysis of *p*-Nitrobenzylphosphonate Ion. In an aqueous solution, the absorption maximum of **1** is 290 nm at pH 5 and shifts to longer wavelength (305 nm) with increasing pH (Fig. 1). This shift may be due to an intramolecular charge transfer.5) In an ethanol solution (containing 2 molar equivalents of DBU), this band shifts to shorter wavelength (298 nm). Upon exposure to ultraviolet light, an aqueous solution of dianion of **1** (50 mmol dm^{-3}) rapidly formed a precipitate, which was identified as 1,2-bis(4-nitrophenyl)ethane (**7**). Small amount of **2** was also detected. The quantum yield of C–P bond cleavage based on the yields of **7** and **2** was 0.86. The photolysis products and their quantum yields varied with the solvent (see below). By ^{31}P NMR observation, the quantitative yield of **4** (δ=2.6, H_2O, pH 12) was also observed after 1 h irradiation (Eq. 1).



(**7**) (1)

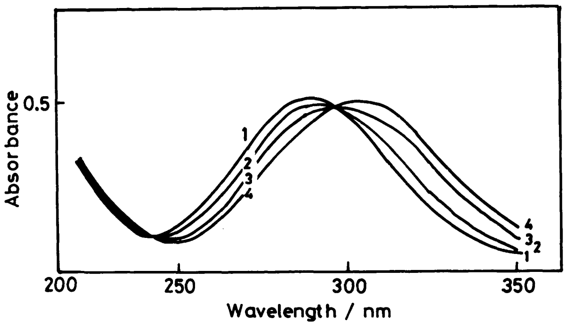
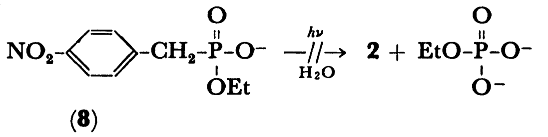


Fig. 1. Absorption spectra of **1** in an aqueous solution (5.0×10^{-2} mmol dm^{-3}) under different pH.
1: at pH ≈5.0, 2: at pH 6.8, 3: at pH 7.2, 4: at pH 8.0≈.

The photolysis of **1** was dependent on pH of the solution (80% EtOH) as shown in Fig. 2. The C–P bond cleavage did not occur below pH 5. It began above pH 5, which corresponds to the concentration of hydronium ion required for second ionization of **1** (pK_a^1 3.9, pK_a^2 9.3 in 80% EtOH). The yields of photolysis products **2** were constant above pH 9 (ϕ=0.76). Ethyl *p*-nitrobenzylphosphonate ion (**8**) did not undergo the C–P bond cleavage even at pH 10 (Eq. 2).


(2)

(**8**)

Our results indicate that the undissociated or monodissociated **1** undergoes no C–P bond cleavage. The complete dissociation of the acid **1** is required for the photo-cleavage of C–P bond. Hammett σ_p constant of phosphono group ($-P(O)(OH)_2$) is 0.29, but that of complete dissociated phosphono group ($-PO_3^{2-}$) is −0.16.⁶⁾ Its electron-donor character increases by the complete dissociation. *p*-Nitrotoluene (**2**) could be produced by the reaction of **5** with H^+. This process is supported by a labelling experiment: The photolysis of $\mathbf{1}^{2-}$ in ethanol-*d*/deuterium oxide (v/v=3/2) gave *p*-nitrotoluene-*α*-*d* as a main product (81%). No phosphonic acid ($HPO(OH)_2$), resulted by homolytic C–P bond cleavage, could be detected by ^{31}P NMR observation of both the irradiated aqueous and ethanolic solutions of **1**. This photolysis was essentially the same in the presence or absence of oxygen: The yield of **4** was not be affected under bubbling of oxygen, although the yield of **2** was slightly reduced owing to a formation of *p*-nitrobenzaldehyde. Consequently, we conclude that the photolysis dose not proceed via radical mechanism, but via heterolytic C–P bond cleavage: The photoexcited **1** dianion may undergo heterolytic C–P bond cleavage to give **5** and **6**. The constancy of quantum yield of C–P bond cleavage with differences in the concentration of **1** also provides an evidence in favor of a direct C–P bond cleavage.

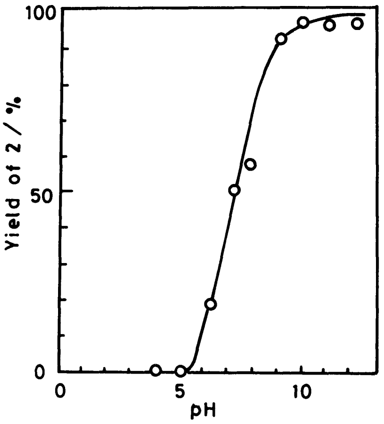


Fig. 2. Effect of pH on photolysis of **1** in 80% EtOH (50 mmol dm^{-3}, 1 h, in N_2).

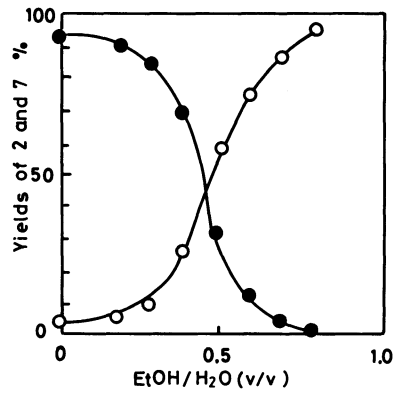


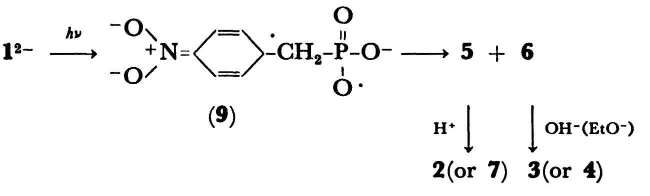
Fig. 3. Change of the product ratio **7**/**2** by the ratio of $EtOH/H_2O$ (**1**, 50 mmol dm^{-3}, pH 10, 1 h, in N_2). —●—: **7**, —○—: **2**.

The product ratio of **7**/**2** decreased with an increase of the ratio of ethanol/water as shown in Fig. 3. In an anhydrous ethanol solution of **1** (containing 2 equivalents of DBU) only **2** was given (ϕ=0.50). The mechanism for the formation of **7** is not clear, and it is being investigated in more detail in our laboratory. The formation of product **7** via **5** by action of strong base on **2** in aqueous solution was reported by other investigator.⁷⁾

Transient Intermediates. Although it is conceivable as an alternative path that **5** is formed by rapid electron transfer from phosphoranyl radical to benzyl radical after homolytic C–P bond cleavage, we can exclude this possibility by the results obtained with laser flash photolysis. The presence of two transient species was revealed by flash photolysis of an aqueous solution of $\mathbf{1}^{-2}$ with 15 ns flash of 308 nm light (Fig. 4). One is a transient species having absorption maximum at 360 nm, which is in agreement with that of **5** reported by Miller and Pobiner from the reaction of **2** with potassium *t*-butoxide in *t*-butyl alcohol.⁸⁾ The absorbance of the transient species was constant above pH 9, but below this was dependent upon the pH and at pH 5 could not be observed. The decrease of its absorbance may be comparable with the decrease of concentration of dianion of **1**. The difference of yields of the transient species in the presence or absence of oxygen was within experimental error. These results are consistent with the results from product analysis. The rate of formation of this absorption band followed first-order kinetics and the rate constant was $1.2\times10^7\ s^{-1}$ in aqueous solution (5.0×10^{-5} mol dm^{-3}, pH 12). The formation rate constant was not affected by the change of pH. In ethanol solution, the absorption maximum was identical with that in an aqueous solution, but the formation rate constant reduced to $0.5\times10^7\ s^{-1}$. The lifetime of this transient species was very long and the decay behavior could not be followed by the ns-flash photolysis technique.

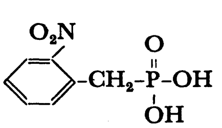
The other short-lived transient having absorption maximum at about 300 nm was also observed, although it could not be analyzed accurately, because the absorption maximum overlapped with that of **1** dianion (305 nm) (Fig. 4). This absorption band decayed together with an weak and broad absorption band at 500—800 nm. The decay rate of the latter band followed first-order kinetics and its rate constant was about $5.8\times10^6\ s^{-1}$. The decay of this transient absorption band may be correlated with the formation of 360-nm band, although there was a small difference in their rate constants. Thus, this short-lived transient intermediate may be a precursor of the 360-nm band and assigned as a diradical dianion **9** resulted by intramolecular electron transfer from PO_3^{2-} to nitro aromatic moiety (Scheme 2). Nagakura, et al. reported that radical anion of **2** has the absorption maxima at 302, 607, and 875 nm in THF.[10]

In an aqueous solution, the decay of 360-nm absorption band after short time exposure (2 s) of ultraviolet light with a high pressure mercury lamp could be observed with moderately high speed scanning using a UV spectrometer (Fig. 5). The lifetime was about 60 s, which is similar to that reported by Margerum (53 s) under the similar reaction conditions.[9] The rate constant for its absorption decay followed second-order kinetics.

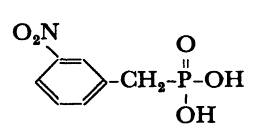


Scheme 2.

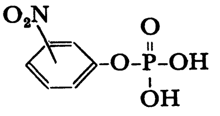
Photolysis of Other Nitrobenzylphosphonate Ions. Dianions of *o*- (**10**) and *m*-nitrobenzylphosphonic acids (**11**) also exhibited a clearly promoted reactivity on illumination, but their photochemical reactivities were more less than that of *p*-derivative (Table 1). Our results do not follow the photochemical patterns observed by Havinga et al., in the solvolysis of *m*- and *p*-nitrophenyl phosphates,[11] or by Zimmerman and Somasekhara, in the solvolysis of *m*- and *p*-nitrophenyl trityl ethers:[12] Readier C-P bond cleavage of **1** do not fit the mechanisms of Zimmerman on photolysis of nitrophenyl phosphates (**12**) in which the excited state of a *m*-nitro structure is considered to be favorable and that of a *p*-nitro unfavorable, for heterolytic cleavage.[13] Other different photochemical behavior of **12** is that the bond cleavage occurs with a definite efficiency between pH 5 and 12.[11]



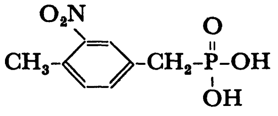
(**10**)



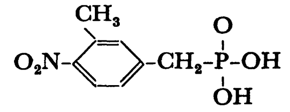
(**11**)



(**12**)



(**13**)



(**14**)

Whereas absorption maximum of *p*-derivatives of **12** in a basic aqueous solution is 310 nm, this band did not shift by increasing pH from 5 to 12. This fact indicates that there is no or little intramolecular charge transfer between PO_3^{-2} and nitro aromatic moiety in **12**. The electronic structure of photoexcited

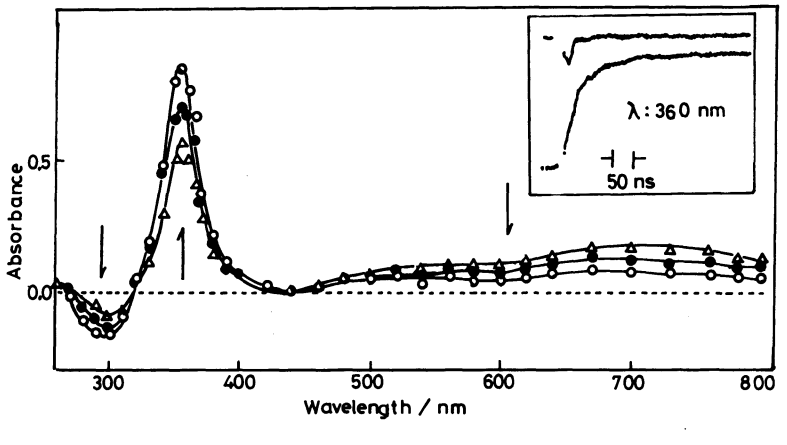


Fig. 4. Flash photolysis spectra from **1** in an aqueous solution (5.0×10^{-2} mmol dm^{-3}, pH 12, in Ar). —△—: After 50 ns, —●—: after 100 ns, —○—: after 300 ns.
The insert figure shows a profile of the formation of transient absorption at 360 nm.

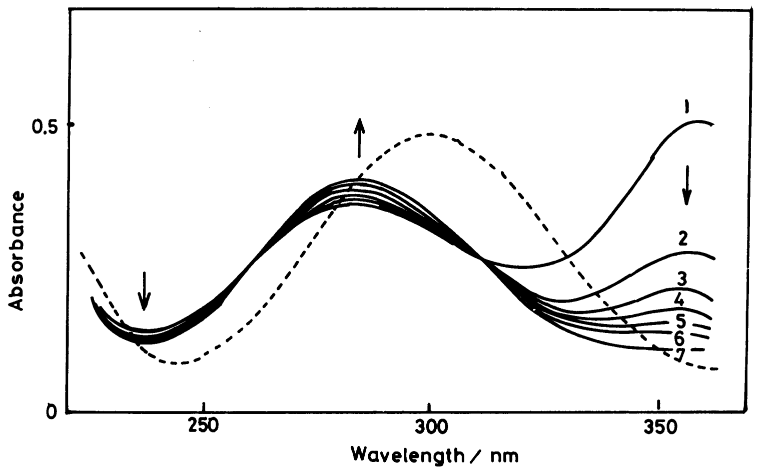


Fig. 5. Change of absorption spectra of **1** in an aqueous solution (5.0×10^{-2} mmol dm^{-3}, pH 12, in N_2) after 2 s irradiation with a high pressure mercury lamp (350 W).
……: Unirradiated, 1: after 20 s, 2: after 50 s, 3: after 80 s, 4: after 120 s, 5: after 150 s, 6: after 300 s, 7: after 500 s.

Table 1. Quantum Yields of C–P Bond Cleavage of the Dianions of **11**, **10**, **1**, and *o*-, *m*-, and *p*-Nitrophenyl Phosphate (**12**)

Compound	Quantum yield
o-Nitrobenzylphosphonate dianion (**11**$^{-2}$)	0.024[a]
m-Nitrobenzylphosphonate dianion (**10**$^{-2}$)	0.039[a]
p-Nitrobenzylphosphonate dianion (**1**$^{-2}$)	0.76[a]
o-Nitrophenyl phosphate dianion	0.003[b]
m-Nitrophenyl phosphate dianion	0.05[b]
p-Nitrophenyl phosphate dianion	0.002[b]

a) Concentration 50 mmol dm^{-3}, 50% EtOH/H_2O, pH 12. b) The aqueous solutions of **12** (0.2 mmol dm^{-3}, 10 mmol dm^{-3} NaOH) were irradiated with monochromatic light of 313 nm.[11]

1 dianion may be entirely different from that of **12** anion. It is well-known that intermolecular electron transfer from an electron donor to *p*-nitrobenzyl chloride give *p*-nitrobenzyl chloride radical anion, which undergoes homolytic bond cleavage to afford *p*-nitrobenzyl radical and chloride anion.[14] In these reaction, numerious instances of light effects have been found, and some of them very large.[15] The fact that the dianion of **10** underwent C–P bond cleavage at a rate one-tenth that of **1** is readily understood in view of Geske's report that *o*-nitrotoluene is significantly more difficult to be reduced than **2**.[16] This is reasonably assumed to be due to steric hindrance to coplanarity in the ortho isomer, which lowers the reducibility of the system by tending electronically to isolate the nitro group from the ring.

Under identical photolysis conditions, dianions of (3-methyl-4-nitrophenylmethyl)phosphonic acid (**13**) and (4-methyl-2-nitrophenylmethyl)phosphonic acid (**14**) hardly underwent C–P bond cleavage.

These behaviors of photochemical C–P bond cleavage of **1** are similar to those of photochemical decarboxylation of nitrophenylacetate ions.[9]

Experimental

All mp and bp were uncorrected. Following spectrometers were used for spectral measurements: UV: Hitachi 323; Excimer laser Lambda Physik EMG 501; ^{1}H and ^{31}P NMR: Bruker WM 360.

Materials. Ethanol and other solvents were dried and distilled by the usual methods.

***p*-Nitrobenzylphosphonic Acid (1):** The acid **1** was prepared by the procedure reported previously.[3] Mp 230—232 °C. UV$_{max}$ (H_2O, pH 12) 305 nm (ε 10,500). ^{1}H NMR (D_2O, DSS, pH 12) δ=2.98 (2H, d, J_{PH}=20 Hz), 7.1—8.1 (m, 4H). ^{31}P NMR (H_2O, 80% H_3PO_4, pH 12) δ=15.2 (t, J_{PH}=20 Hz).

***o*-Nitrobenzylphosphonic Acid (10):** After an equimolar mixture of *o*-nitrobenzyl bromide and triethyl phosphite was refluxed for 1 h, the mixture was distilled to give diethyl *o*-nitrobenzylphosphonate. Bp 160—165 °C/0.1 mmHg.† It was hydrolyzed by refluxing with hydrobromic acid for 12 h. The hydrolyzed acid **10** was recrystallized from water. Mp 190—191 °C, UV$_{max}$ (H_2O, pH 12) 270 nm (ε 6,600). ^{1}H NMR (D_2O, DSS, pH 12) δ=3.65 (2H, d, J_{PH}=22.0), 7.1—8.0 (4H, m). Found: C, 38.56; H, 3.69; N, 6.58; P, 14.12%. Calcd for $C_7H_8NO_5P$: C, 38.72; H, 3.71; N, 6.45; P 14.27%.

***m*-Nitrobenzylphosphonic Acid (11):** The acid **11** was prepared by the same method as described above. Diethyl *m*-nitrobenzylphosphonate, bp 186—187 °C/0.5 mmHg, **11**, mp 186—187 °C. UV$_{max}$ (H_2O, pH 12) 280 nm (ε 7,300). ^{1}H NMR (D_2O, pH 12) δ=2.84 (2H, d, J_{PH}=18.0 Hz), 7.1—8.0 (4H, m). Found: C, 38.81; H, 3.68; N, 6.38; P, 12.41%. Calcd for $C_7H_8NO_5P$: C, 38.72; H, 3.71; N, 6.45; P, 12.63%.

Ethyl *p*-Nitrobenzylphosphonate (8): The phosphonate **8** was prepared by nitration of ethyl benzylphosphonate with fuming nitric acid at 0 °C. Ethyl benzylphosphonate (mp 63—64 °C) was prepared by partial hydrolysis of diethyl

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† 1 mmHg=133.3 Pa.

benzylphosphonate with 1 mol dm^{-3} NaOH 50% ethanol solution. **8**, mp 156—157 °C. UV$_{max}$ (H_2O, pH 12) 290 nm (ε 10,600). ^{1}H NMR (D_2O, DSS, pH 12) δ=1.17 (t, 3H, J_{HH}=7.0 Hz), 3.10 (d, 2H, J_{PH}=20 Hz), 3.80 (quint, 2H, J_{HH}=7.0 Hz), 7.3—8.2 (m, 4H). Found: C, 44.25; H, 5.06; N, 5.69; P, 14.54%. Calcd for $C_9H_{12}NO_5P$: C, 44.09; H, 4.93; N, 5.71; P, 14.40%.

(3-Methyl-4-nitrophenylmethyl)phosphonic Acid (13): *m*-Methylbenzylphosphonic acid was nitrated with a nitric acid–sulfuric acid mixture (v/v=1:3) at 0 °C. Mp 219—220 °C. UV$_{max}$ (H_2O, pH 12) 268 nm (ε 5,100). ^{1}H NMR (D_2O, DSS, pH 12) δ=2.58 (s, 3H), 3.35 (d, 2H, J_{PH}=20 Hz) 7.3—8.4 (m, 4 H). Found: C, 41.48; H, 4.27; N, 6.21; P, 13.37%. Calcd for $C_8H_{10}NO_5P$: C, 41.57; H, 4.36; N, 6.06; P, 13.40%.

(4-Methyl-3-nitrophenylmethyl)phosphonic Acid (14): *p*-Methylbenzylphosphonic acid was nitrated as described above. Mp 209—210 °C, UV$_{max}$ (H_2O, pH 12) 274 nm (ε 3,800). ^{1}H NMR (D_2O, DSS, pH 12) δ=2.37 (s, 3H), 2.92 (d, 2H, J_{PH}=19 Hz), 7.0—8.0 (m, 3H). Found: C, 41.39; H, 4.18; N, 6.21; P, 13.49%. Calcd for $C_8H_{10}NO_5P$: C, 41.57; H, 4.36; N, 6.06; P, 13.40%.

Product Identification. The insoluble product was separated from the photolyzed aqueous solution of **1** by extraction with chloroform. The chloroform extract was evaporated, and the residue was recrystallized from acetone–ethanol to give **7**, pale yellow-needle (mp 181—183 °C) and it was identified by GLC with an authentic sample.

From a photolyzed ethanol solution of **1**, **2** was isolated. The ethanol was evaporated, and the residue was recrystallized from water–ethanol to give **2** (mp 51—52 °C), and identified by GLC with an authentic sample.

Typical Procedure of Photolysis. Five ml of a 50% ethanol solution of **1** (50 mmol dm^{-3}) was adjusted at pH 12 with a 10% aqueous solution of sodium hydroxide. Nitrogen was bubbled through the solution before irradiation. The solution was irradiated in a Pyrex tube (ϕ=10 mm) with a high-pressure mercury lamp (350 W) for 1 h under cooling with running water. The progress of the photolysis was directly monitored by a GLC analysis using biphenyl as an internal standard [Silicone OV-17 (2%) on Chromosorb W AW DMCS] of **2** or **7**. When the photolysis in a aqueous solution was carried out, chloroform (5 ml) was added and the mixture was shaken sufficiently. Analyses were performed on the chloroform extracts.

Photolysis of 1 in the Presence of Oxygen. The 80% ethanol solution of **1** (50 mmol dm^{-3}, pH 12) was irradiated in the same manner described above. Oxygen was bubbled into the solution during the irradiation. After irradiation, the solution was directly analyzed by GLC. *p*-Nitrobenzaldehyde, other than **2**, has been detected by comparison with an authentic sample (5.2%). As another oxidation product, a trace amount of *p*-nitrobenzyl alcohol was also detected.

Photolysis of 1 in Ethanol-*d*/Deuterium Oxide. One ml of ethanol-*d*/deuterium oxide solution (v/v=3/2) of **1** (50 mmol dm^{-3}) containing two equivalents of sodium deuteroxide was irradiated in the same manner as described above. The product was extracted with chloroform-*d*, and the extract was subjected to ^{1}H NMR analysis. *p*-Nitrotoluene-α-*d* [^{1}H NMR ($DCCl_3$, TMS) δ=2.46 (t, 2H, J_{DH}=2.2 Hz), 7.3—8.1 (m, 4H)] content in the product was 81%. When the ethanol-*d*/deuterium oxide solutions of **1** and **2** were allowed to stand for 24 h without UV-irradiation, isotopic hydrogen exchange on the methylene and the methyl groups of them could not be observed.

Measurement of the Quantum Yield. The quantum yields were determined on the basis of generated nitrotoluene and/or **7**, and chemical actinometry using 2-hexanone. The sample solutions (50 mmol dm^{-3}) were irradiated in a merry-go-round apparatus employing 313-nm monochromatic light according to the procedures previously described.[4)]

Flash Photolysis. Flash photolyses were carried out by using a XeCl excimer laser Lambda Physik EMG 501 supplying 15 ns pulses of 308 nm light (energy 100 mJ/pulse). The solutions of **1** (5×10^{-2} mmol dm^{-3}, pH 12) were prepared freshly before irradiation and were deoxygenated by bubbling with argon gas. Irradiated solutions were replaced by a fresh solution for each pulse. The transmissions of samples were monitored using an optical system consisting of Xe-pulse lamp (Osram OPG 450), a monochromater (Nikon G-250), and a photomutiplier tube (Hamamatsu Photonics R928).

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