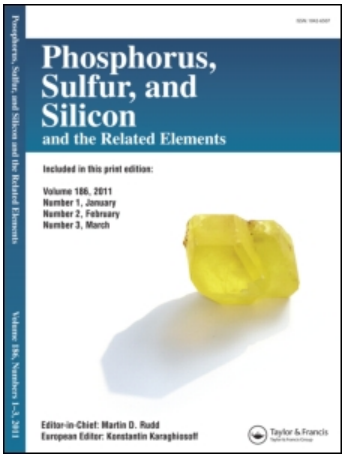

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Yoshiki Okamoto[a]; Toshiki Sikata[a]; Setsuo Takamuku[a]
[a] The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, Japan

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PHOTOCHEMICAL C–P BOND CLEAVAGE OF BENZOYLBENZYLPHOSPHONIC ACIDS

YOSHIKI OKAMOTO,* TOSHIKI SIKATA and SETSUO TAKAMUKU
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567 Japan

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Benzoylbenzylphosphonic acids (*p*- and *m*-) easily underwent photochemical C–P bond cleavage in a basic aqueous ethanol solution to give methylbenzophenone, orthophosphate, and ethyl phosphate.

INTRODUCTION

Although the C–P bond cleavage of alkylphosphonic acid dialkyl esters is well-known in the Horner–Emmons and relate reactions,[1] the C–P bond cleavage of alkylphosphonic acids is unfamiliar. The C–P bond of the acid is generally stable under acidic or basic conditions except for a few examples. The C–P bond of (β-haloalkyl)-phosphonic acid cleaves in an alkaline aqueous solution to give olefin and metaphosphate anion, which reacts with water immediately to afford phosphate anion (Conant–Swan reaction).[2] Having a reported on the photochemical O–P bond cleavage of *m*-nitrophenyl phosphate,[3] which was applied to the preparation of alkyl phosphates,[4] and to a photosensitive protecting group for phosphate esters[5]. However there is no example of the photochemical C–P bond cleavage of a phosphonic acid. Recently, the photochemical C–P bond cleavage of *p*-nitrobenzylphosphonic acid in an alkaline solution has been reported.[6] This reaction is of interest as a new source of monomeric metaphosphate anion.[7] In this report, we wish to report the photochemical C–P bond cleavage of (benzoylbenzyl)phosphonic acid (**1**), which was quite stable in the dark.

RESULTS AND DISCUSSION

In an aqueous solution, the absorption maximum of (*p*-benzoylbenzyl)phosphonic acid (**1a**) has λ max 273 nm (ε 18,300) at pH 5 and shifts to higher wavelength with increasing pH (283 nm, ε 18,000 at pH 10). Upon irradiation of **1a** in a basic solution at room temperature, the C–P bond cleaved to give 4-methylbenzophenone (**2a**), and orthophosphate in almost quantitative yields, respectively. The efficiency of this bond cleavage depends on the pH of the solution as shown in Figure 1. The bond cleavage began above pH 8, and the quantum yield of **2a** reached 0.40 at pH 9.0. This suggests that complete dissociation of the acid is required for the bond cleavage. The Hammett σ_p constant of the phosphono group (—P(O)(OH)$_2$) is 0.29, but that of the completely dissociated phosphono group (—PO_3^{2-}) is −0.16.[8] Its electron-donor

* Author to whom all correspondence should be addressed.

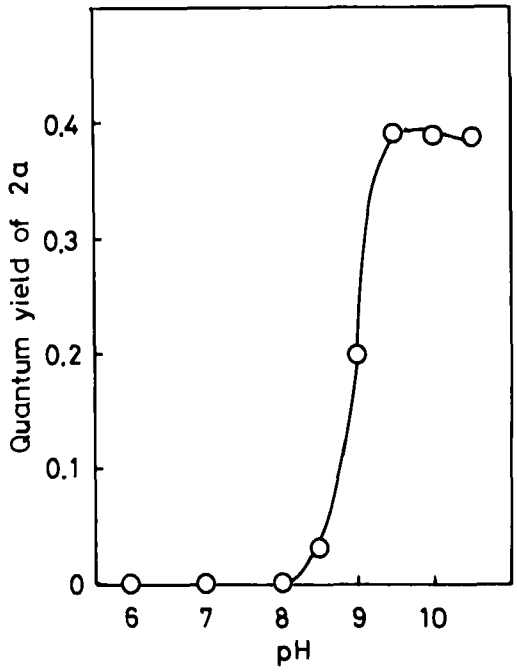


FIGURE 1 Plot of quanum yield for the formation of **2a** as a function of pH of the aqueous solution of **1a** (2.5×10^{-2} mol dm^{-3}).

character increases with the completeness of dissociation. The C–P bonds of the diethyl ester and monoethyl ester of **1a** did not cleave. The presence of oxygen did not affect the results of photolysis of **1a**. The photolyses of **1a** in water, 80% ethanol, or 80% isopropanol gave similar results (quantum yields 0.40, 0.36, and 0.36, respectively). Photolysis of **1a** in ethanol-O-D/deuterium oxide gave 4-methylbenzophenone-α-D and **2a** at the ratio of 93/7. These results show that the bond cleavage took place in a heterolytic manner.

The presence of two transient species was revealed by laser flash photolysis of an aqueous solution of $\mathbf{1a}^{2-}$ with a 15 ns flash of 308 nm light (Figure 2). One of the transition species had a broad absorption band in the range of 400–800 nm, and it decayed with a first-order rate constant of 2.3×10^6 s^{-1}. Another species having an absorption maximum at 400 nm formed with a first-order rate constant of 4.6×10^6 s^{-1}. The lifetime of the latter transient species was so long that the decay behavior could not be followed by the ns-flash-photolysis technique. The former species ($[\mathbf{1a}^{2-}]^*$) may be a precursor of the latter. Although the identification of these absorption bands has remained obscure, the latter absorption band seems to be that of benzoylbenzyl anion (**3a**). It is conceivably formed by the path described in Scheme 1, in which benzoylbenzyl anion (**3a**) formed via photochemically heterolytic C–P bond cleavage of $\mathbf{1a}^{2-}$ may be involved.

Meta derivatives also gave similar results (quantum yield 0.34).

Upon irradiation of **1a** in an excess amount of absolute ethanol in the presence of twice-molar amounts of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), ethyl phosphate was the sole product in 91% yield (quantum yield 0.04).

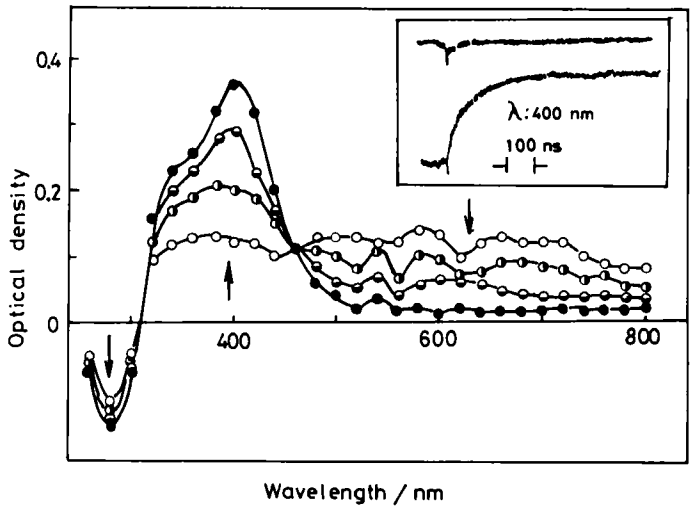
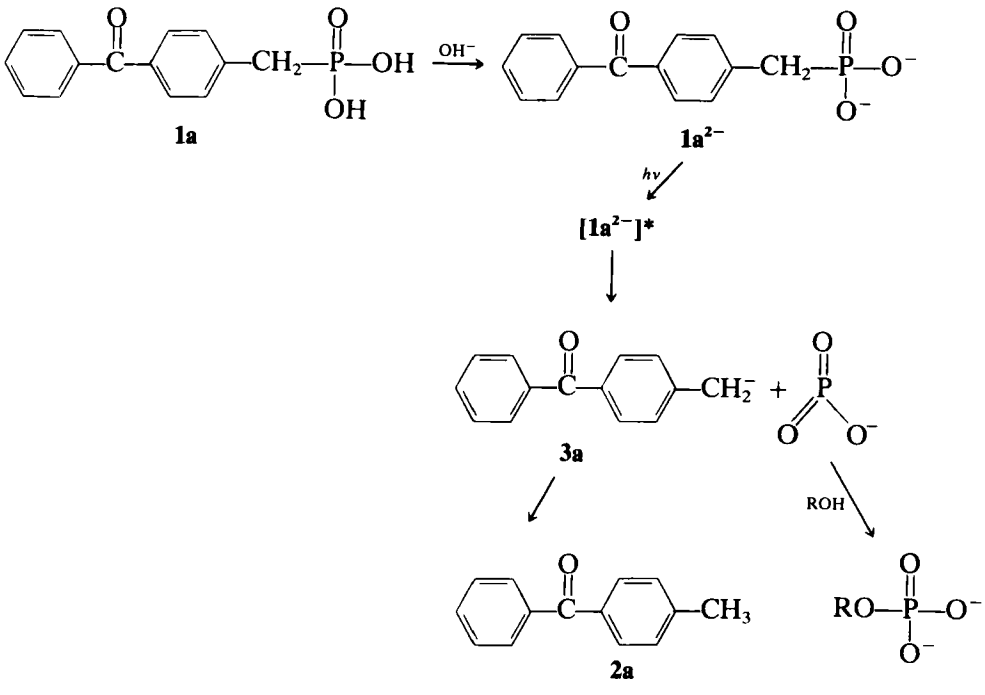


FIGURE 2 Transition absorption spectra by flash photolysis of the aqueous solution of **1a** (1.3×10^{-4} mol dm^{-3}, pH 12, in Ar). ○: After 40 ns, ◑: after 100 ns, ◒: after 200 ns, ●: after 500 ns.



1a **1a²⁻** **[1a²⁻]*** **3a** **2a**

SCHEME 1

EXPERIMENTAL

^{31}P nmr spectra were recorded on a Bruker WM 360 instrument using $PPh_3/DCCl_3$ as an external reference. Signals downfield of H_3PO_4 are quoted as positive in line with the current convention. UV

spectra were recorded on a Hitachi, 150-20. Excimer laser Lambda Physik EMG 501 was used for laser flash photolysis.

Preparation of (p-benzoylbenzyl)phosphonic acid (**1a**). 4-Methylbenzophenone (**2a**) was brominated in carbon tetrachloride with an equimolar amount of bromine under irradation of a tungsten lamp at refluxing temperature for 1 h. The reaction mixture was distilled to give (4-bromomethyl)benzophenone. A mixture of triethyl phosphite (9.1 g, 55 mmol) and (4-bromomethyl)benzophenone (14.2 g, 50 mmol) was heated at 120°C for 1 h and distilled to give diethyl (*p*-benzoylbenzyl)-phosphonate (8.9 g, 53.6%, b.p. 220–225°C/0.1 mm). The ester (5.0 g, 15 mmol) was hydrolyzed by refluxing with 200 ml of 6 mol dm^{-3} hydrochloric acid for 6 h and the mixture was evaporated to dryness on a water bath by means of an aspirator. The residue was recrystallized from water to give pure **1a**. Yield 3.5 g (84%) m.p. 188–190°C, Anal. found: C, 61.07; H, 4.66; P, 11.03%. $C_{14}H_{13}PO_4$ requires; C, 60.87, H, 4.74; P, 11.23%. ^1H nmr (D_2O/DSS, pH 12) δ (ppm) 3.02 (2H, d, J_{HP} = 22.0 Hz), 7.2–7.6 (9H, m). UV (H_2O, pH 12) λ max 285 (ε 18,300). pK_a^1 3.0, pK_a^2 8.5 (50% ethanol).

Preparation of (m-benzoylbenzyl)phosphonic acid (**1b**). **1b** was synthesized in the manner described above. Diethyl (*m*-benzoylbenzyl)phosphonate; b.p. 212–217°C/0.1 mm. **1b**; m.p. 150–151°C. Anal. found: C, 60.59; H, 4.56; P, 11.17%. $C_{14}H_{13}PO_4$ requires; C, 60.87; H, 4.74; P, 11.23%. ^1H nmr (D_2O/DSS, pH 12) δ (ppm) 3.00 (d, 2H, J_{HP} = 19.0 Hz), 7.2–7.7 (9H, m). UV (H_2O, pH 12) λ max 265 nm (ε 15,500). pK_a^1 3.5, pK_a^2 9.0 (50% ethanol).

Photolysis of **1a** *and* **1b** *in 50% ethanol solution* Five ml of 50% ethanol solution of **1** (50 mmol dm^{-3}) was adjusted at pH 10 with a 10% aqueous solution of sodium hydroxide. Argon 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 of the products using biphenyl as an internal standard [Silicone OV-17 (2%) on Chromosorb W AW DMCS]. The product was identified as **2** by comparison with GLC retention times of the authentic sample. On further irradiation, the yields of methylbenzophenone decreased and other unknown products were formed. ^{31}P nmr analysis of the photolysis mixture revealed the presence of only two species of phosphorus compounds; one was orthophosphate (δ = 3.6 ppm), and the other was unreacted **1a** (δ = 16.1 ppm, *t*, J_{HP} = 20 Hz).

Photolysis of **1a** *in absolute ethanol* Five ml ethanol solution of **1a** (50 mmol dm^{-3}) containing DBU (100 mmol dm^{-3}) was irradiated in the manner previously described. After irradiation of 1 h, the mixture was employed for a ^{31}P nmr analysis. Only two signals, of ethyl phosphate dianion (δ = 2.1 ppm, *t*, J_{PH} = 7.0 Hz) and unreacted $\mathbf{1a}^{-2}$ (δ = 15.6 ppm, *t*, J_{PH} = 20 Hz), were observed. The yield of ethyl phosphate was calculated from these integral values.

Photolysis of **1a** *in ethanol-O-D/deuterium oxide* One ml of ethanol -O-D/deuterium oxide solution (v/v = 3/2) of **1a** (50 mmol dm^{-3}) containing two equivalents of sodium deuteroxide was irradiated in the manner described above. The product was extracted to ^1H nmr analysis. 4-Methylbenzophenone-α-D [^1H nmr ($DCCl_3$, TMS) δ = 2.43, *t*, J_{HD} = 2.16 Hz] content was 93%. When the ethanol-O-D/deuterium oxide solutions of **1a** or **2a** were allowed to stand for 24 h without UV-irradiation, isotopic hydrogen exchange on their methylene and the methyl groups could not be observed.

Measurement of the quantum yield The quantum yields were determined on the basis of generated **2** and chemical actinometry using 2-hexanone. A 2,2,4-tetramethylpentane solution of 2-hexanone with an absorbance identical with that of the solution of **1** was irradiated in a merry-go-round apparatus employing 313 nm monochromatic light using a filter solution of 0.1% K_2CrO_3-0.1% K_2CO_3. The yields of **2** and acetone were determined by GLC analysis. The quantum yield of acetone formation was taken as 0.25 in 2,2,4-trimethylpentane at room temperture. The photolyses of **1** were carried out with no more than 10% decomposition in order to suppress further reactions of **2**.

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 aqueous solutions of **1a** (1.3×10^{-4} mol 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 a Xe-pulse lamp (Osram OPG 450), a monochromator (Nikon G-250), and a photomultiplier tube (Hamamatsu Photonics R928).

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