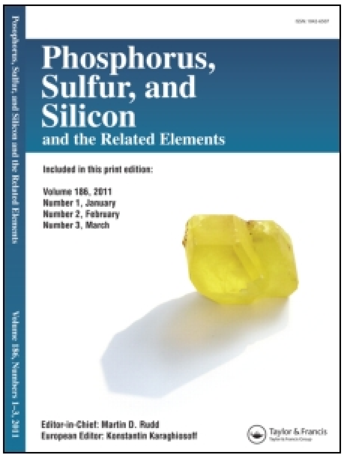

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PHOTOCHEMICAL REACTIONS OF TRI-1-NAPHTHYL AND TRIS(8-QUINOLYL) PHOSPHATES

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

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PHOTOCHEMICAL REACTIONS OF TRI-1-NAPHTHYL AND TRIS(8-QUINOLYL) PHOSPHATES

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

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Upon UV-irradiation in alcohol, tri-1-naphthyl phosphate give 1-naphthyl 1,2′-binaphthalene-1′-yl phosphate and 1,1′-binaphthalene through intramolecular processes. Under the same conditions, tris(8-quinolyl) phosphate give alkyl phosphates by photo-alcoholysis, but in acetonitrile furadiquinoline was given. The reaction mechanisms was investigated by means of quenching experiments for fluorescence spectra and products by oxygen.

Key words: Tri-1-naphthyl phosphate, tris(8-quinolyl) phosphate, reaction mechanism, fluorescence spectra, UV spectra.

INTRODUCTION

It has been reported that upon UV-irradiation tris(4-methoxyphenyl) phosphate or bis(4-methoxyphenyl) methylphosphonate give 4,4′-dimethoxybiphenyl and 2,5,4′-trimethoxybiphenyl via a monomeric singlet excited species and an intramolecular singlet excimer, respectively.[1] It has been also revealed that these unique intramolecular photochemical reactions are characteristic photo-reactions of phosphate, phosphonate or phosphite connecting two aromatic groups by O—P—O linkage. Other substituted phenyl phosphates or alkyphosphonate also react in the similar manner though low reactivity.[2] The similar reaction cannot be observed on the other analogous compounds connecting by O—B—O, O—S—O, O—Si—O, or O—C—O linkage.[2]

In this paper, the photochemical reactions of dinuclear aromatic derivatives, 1-naphthyl (**1**) and 8-quinolyl phosphates (**2**) have been done, and the distinction of reactivity between **1** and **2** was revealed.

RESULTS AND DISCUSSION

Photolysis of Tri-1-naphthyl Phosphate (**1**)

Tri-1-naphthyl phosphate is hardly soluble in methanol at ambient temperature, and therefore, the photolysis was carried out in acetonitrile (1.0×10^{-3} M) under the argon atmosphere. The solution was irradiated with a high pressure Hg lamp for 20 min (conversion 26%). The reaction mixture was analyzed with GLC-MS after methylation with diazomethane. Methyl 1-naphthyl 1,2′-binaphthalene-1′-yl phosphate (**3**) (yield 46%, quantum yield $\phi = 0.013$), 1,1′-binaphthalene (**4**) (1.2%), and dimethyl 1-naphthyl phosphate (**5**) (trace) were obtained (Scheme I). These compounds were confirmed by comparison with authentic samples or by ^1H and ^{13}C-NMR spectrometer after isolation with silica gel chromatography as described below.

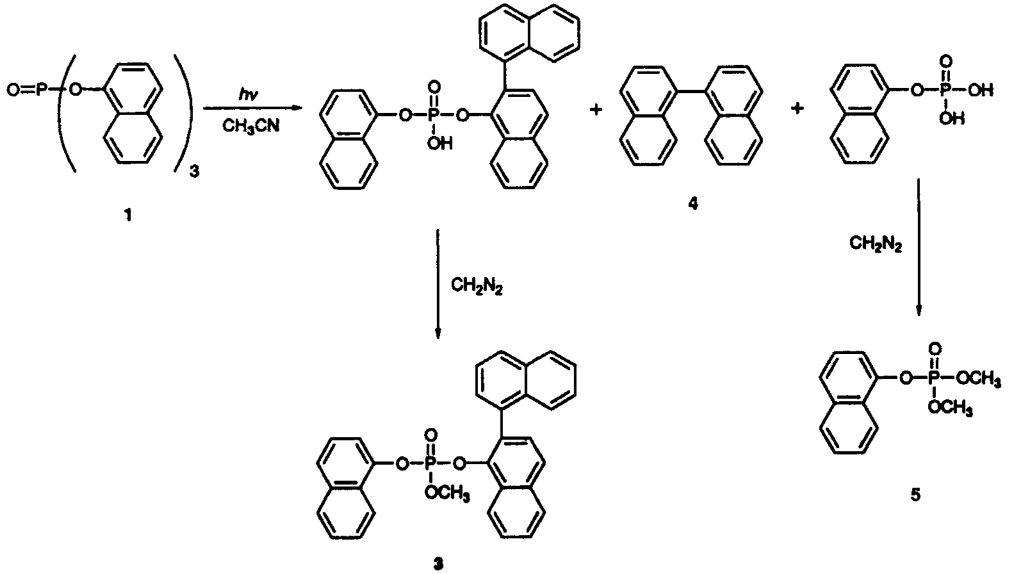
Photolysis of the saturated solution of **1** in acetonitrile containing 20% methanol gave the same products, though the yields were low and scattered.

*Photolysis of Tris(8-quinolyl) Phosphate (**2**)*

Tris(8-quinolyl) phosphate (**2**) has been used as a phosphorylating reagent of natural alcohols in basic media.[3,4] But at ambient temperature **2** is stable in ethanol. Upon exhaustive UV-irradiation **2** completely solvolyzed to give triethyl phosphate (**6**) and 8-quinolinol (**7**). The quantum yield of the consumption of **2** was 0.012. The formation of intermediates of solvolysis, ethyl bis(8-quinolyl) phosphate (**8**) and diethyl 8-quinolyl phosphate (**9**), were also observed under moderate irradiation. When solvolyses with other alcohols were carried out, the corresponding alkyl phosphates were obtained, respectively. The reactivity order is MeOH (consumption of **2** after 30 min at 18°C; 46%) > EtOH (35%) > BuOH (24%).

Upon UV-irradiation in acetonitrile (1.0×10^{-3} M) under argon atmosphere, fura[2,3,-f:4,5-f′] diquinoline (**10**) was given, whose quantum yield was 0.0065, and the formation of a trace amount of unknown product was also observed.

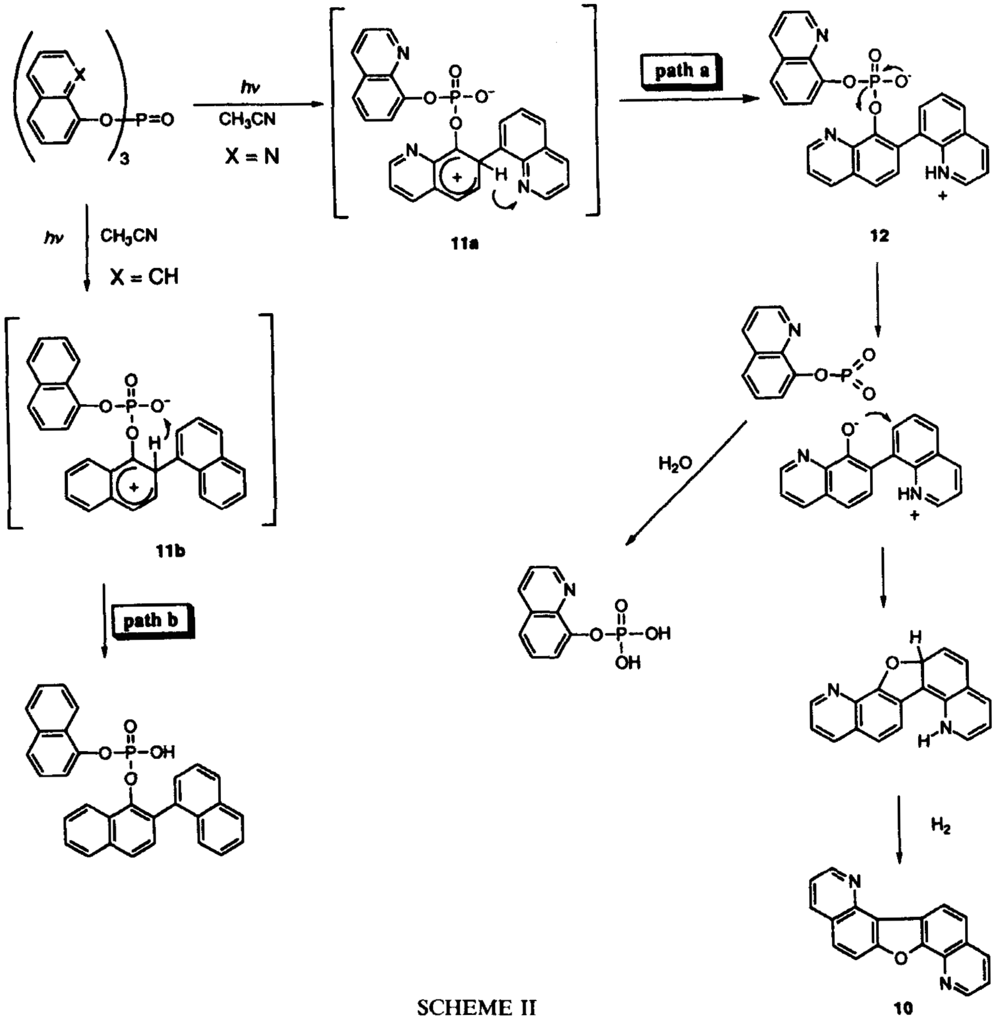
The difference of the reactivities between **1** and **2** in acetonitrile may result from participation of basic nitrogen atom in a quinolyl group. The primary reaction process of photo-excited triaryl phosphate may be intramolecular electrophilic 1,6-rearrangement of an aryl group. In the case of **2**, the proton transfers from the



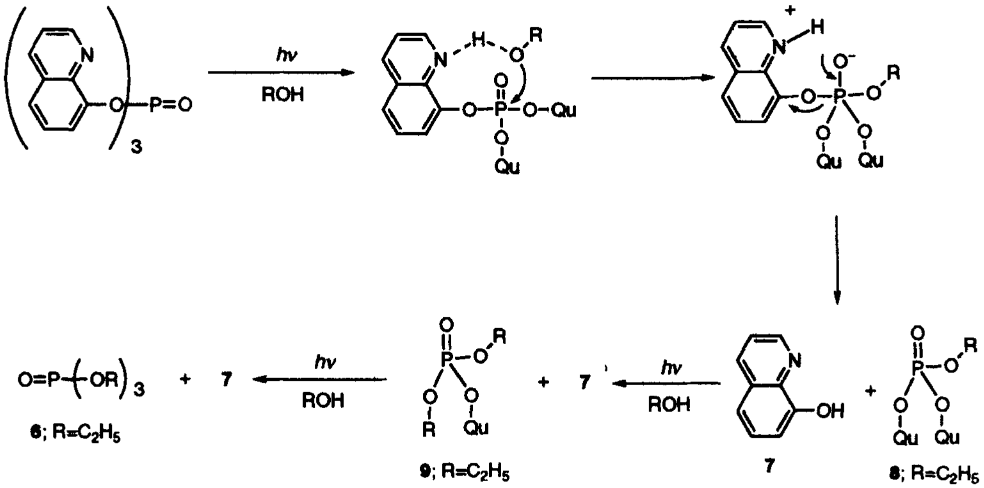
SCHEME I

arenium type ion **11a** to nitrogen atom of quinolyl ring to give the quinolinium type ion **12**, which may be received with further electrophilic attack of the quinolyloxy anion to the neighboring quinolyl ring to give **10** (path a). On the other hand, the proton of arenium ion **11b** produced from **1** migrates to anionic phosphoryl oxygen to give **3** (path b) (Scheme II). It had been reported that dibenzofurane was given by pyrolysis of triphenyl phosphate at the presence of magnesium oxide.[5]

In alcoholic solution, the nucleophilic attack of alcohol to phosphorus atom occur predominantly in quinolyl phosphate than in naphthyl phosphate by photo-irradiation, because the electrophilicity of phosphorus atom may be more increased by a photo-excited quinolyl group than the naphthyl group. Neighboring group participation of nitrogen atom may have also assisted the nucleophilic attack of alcohol by detachment of the proton (Scheme III).



SCHEME II



SCHEME III

Fluorescence Spectra

Fluorescence spectra of **1** is shown together with a spectra of dimethyl 1-naphthyl phosphate **5** as a reference of monomeric phosphate in Figure 1. The large emission band of 1 was different from that of **5**, which shifted to the longer wavelength. The band (385 nm) was ascribed to that of the intramolecular excimer and its lifetime was 14.4 ns. It could not be disclosed whether a monomeric emission band is contained or not. The emission band of **2** was similar to that of **9**, and therefore the band was attributable to only a monomeric emission band. An excimer emission band could not be observed (Figure 2).

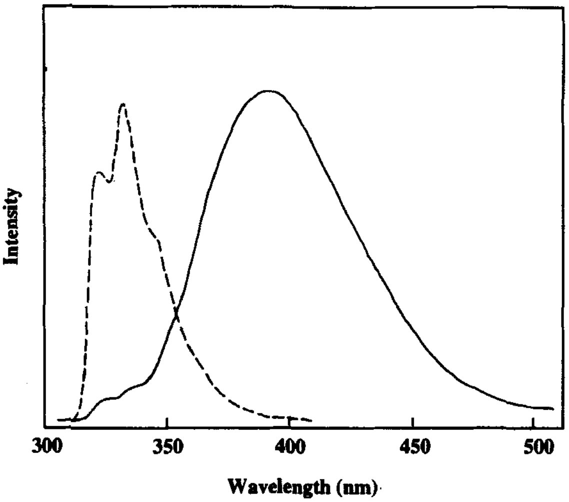


FIGURE 1 Fluorescence spectra of **1** (solid) and **5** (broken) in acetonitrile (1.0×10^{-4} M, λ_{ex} = 280 nm).

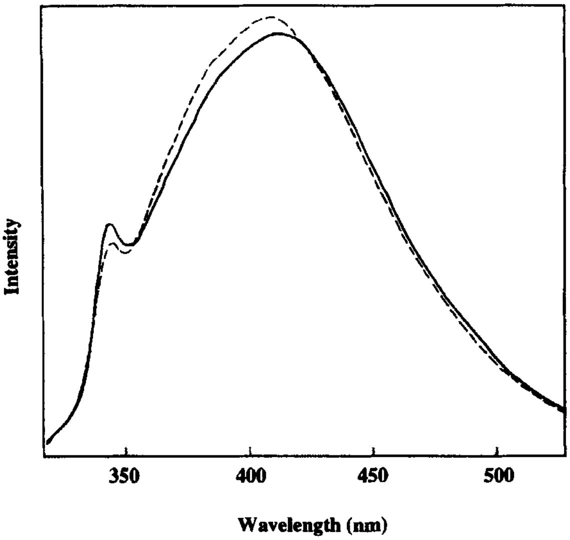


FIGURE 2 Fluorescence spectra of **2** (solid) and **9** (broken) in ethanol (1.0×10^{-4} M, $\lambda_{ex} = 280$ nm).

Quenching Experiment by Oxygen

Both fluorescence intensity and product yield were quenched by oxygen. A linear correlation between fluorescence intensity of **1** and oxygen concentration was obtained in MeCN. A value of $k_{qf}\tau_f$ was calculated from the slope of this line as 271 M^{-1} (Stern-Volmer analysis),[6]

$$I_f^0/I_f = 1 + k_{qf}\tau_f[O_2]$$

where I_f and I_f^0 are the intensity of fluorescence at the presence and the absence of oxygen, k_{qf} is the rate constant of fluorescence quenching by oxygen, and τ_f is a lifetime of the fluorescence (singlet excited stated). The τ_f value was determined as 14.7 ns by single photon counting method, and then k_{qf} was 1.8×10^{10} s^{-1}, which is a reasonable value as a diffusion controlled rate constant in MeCN.[7]

Although the product quenching experiment for **1** was tried, a linear correlation could not be obtained. The data were scattered because the accurate estimate of the product yield was difficult.

The similar quenching experiment for **2** in EtOH was performed. From the fluorescence quenching experiment, a value of $k_{qf}\tau_f$ was determined as 73 M^{-1}, while from conversion quenching experiment a value of $k_{qp}\tau_p$, was determined as 79 M^{-1}. Both values were nearly agreed with each other. Therefore, the photosolvolysis of **2** in EtOH may proceed via a singlet excited state. If there is more than one excited state (singlet and triplet species) in solvolysis of **2**, the linear relationship between conversion quantum yield and oxygen concentration could not be obtained.

EXPERIMENTAL

Apparatus

Melting points were obtained with a Yanagimoto micropoint apparatus. CHN microanalyses were obtained with a Perkin-Elmer Model 240 analyzer. UV-visible spectra were recorded with a Hitachi 150-20 spectrometer. Steady-state fluorescence spectra were recorded with a Hitachi 850 type fluorescence spectrometer, and fluorescence lifetime was measured by the time-correlated, single-photon-counting method using a Horiba NAES-1100 time-resolved fluorescence spectrometer. ^{1}H- and ^{13}C-NMR spectra were determined in $CDCl_3$ with tetramethylsilane as an internal standard on a Bruker-AM600 spectrometer. ^{31}P-NMR spectra were determined in $CDCl_3$ with 80% H_3PO_4 as an external standard on JEOL FX 90Q spectrometer. GLC analyses were carried out by use of a 2% Silicone OV-17 on Chrom. GC-MS spectra were recorded with a JMS-DX 300 and high-resolution mass spectra were also obtained on a JMS-01SG-2 instrument. HPLC analyses were carried out by use of a Shimadzu LC-10AS instrument with a column of Shiseido CAPCELL PAK C18 AG 120. Photolysis were carried out with a 300 W high pressure mercury lamp EHBW-300 (Eikosha Co., Ltd.) and a 60 W low pressure mercury lamp.

Materials

Tri-1-naphthyl phosphate (**1**): Phosphate **1** was prepared by the reaction of phosphorus pentachloride and 1-naphthol in carbon tetrachloride.[8] mp 149–150°C, λ_{max} (MeCN) 271.2 ($\varepsilon = 1.6 \times 10^4$), 280.4 ($1.9 \times 10^4$).

Tris(8-quinolyl) phosphate (**2**): Phosphate **2** was prepared by the reaction of 8-quinolinol with phosphorus oxychloride in 2,4,6-trimethylpyridine.[3,4]

Diethyl 8-quinolyl phosphate (**9**): Phosphate **9** was prepared by the reaction of 8-quinolinol with diethyl phosphoryl chloride at the presence of triethylamine in ether. Purification was done by silica gel column chromatography. Colorless oil (Found: C, 55.41; H, 5.66; N, 4.73; P, 10.95%. $C_{13}H_{16}N_1O_4P_1$ requires: C, 55.52; H, 5.73; N, 4.98; P, 11.01%). ^{31}P NMR ($CDCl_3$; 80% H_3PO_4) $\delta = 6.59$.

General Photolysis Procedure

A 200-cm^3 solution of **1** ($10^{-2} \sim 10^{-3}$ M) was charged in a doughnut type cell of 10 mm thick (quartz) and argon was bubbled through the solution to purge off dissolved air. After irradiation with a high-pressure Hg lamp (300 W) at ambient temperature for 1 h, the reaction products were directly analyzed by HPLC by comparison with authentic samples prepared by other methods. In some cases, after methylation with diazomethane the products were analyzed for GLC or GC-MS. When the isolation of products were necessary, a column chromatography on silica gel was applied, and assignment was carried out with element analysis, ^{1}H, and ^{13}C NMR spectroscopy.

Identification of Photolysis Products from 1

After methylation of the photolyzed product with diazomethane, a direct GC-MS analysis gave two peaks besides the starting material. Their m/z were 250 and 490, respectively. After refluxing the photolyzed product with excess methanol at presence of HCl, two products were also isolated with a silica gel column chromatography, respectively, and each component was identified as follows. *1,1'-Binaphthalene* **4**, mp 152–153°C, which was identified with an authentic sample prepared by the reaction of 1-bromonaphthalene with copper and iodine at 280°C for 4 h. *1,2'-Binaphthalene-1'-ol*, m/z 270 (M^+; 100), 239 (10), 120 (10), etc. ^{13}C NMR ($CDCl_3$; Me_4Si); $\delta = 148.6$, 134.5, 134.3, 134.3, 132.1, 128.9, 128.6, 128.5, 128.3, 127.5, 126.9, 126.6, 126.5, 126.3, 125.9, 125.6, 124.3, 122.6, 119.9, 119.5. ^{1}H ($CDCl_3$; Me_4Si) $\delta = 8.32$ (1H, dd, 9.0, 2.3), 7.95 (1H, d, 8.0), 7.96 (1H, d, 7.0), 7.88 (1H, dd, 8.8, 2.3), 7.68 (1H, d, 7.4), 7.61 (1H, dd, 9.0, 8.9), 7.56 (1H, dd, 7.0, 8.0), 7.55 (1H, d, 6.9), 7.54 (1H, dd, 7.0, 8.0), 7.54 (1H, d, 7.4), 7.53 (1H, dd, 6.9, 7.0), 7.42 (1H, dd, 9.0, 8.8), 7.35 (1H, d, 8.2). By methylation of 1,2'-Binaphthalene-1'-ol with diazomethane, 1-methoxy-1',2-binaphthalene (m/z 284 (M^+; 100), 269 (70), 239 (20), 134 (10), etc) was obtained. Therefore, the primary product was 1-naphthyl 1,2'-binaphthalene-1'-yl phosphate.

Identification of Photolysis Products in Alcohol from **2**

Alkyl diquinolyl phosphate or dialkyl quinolyl phosphates were directly analyzed with HPLC by comparison with authentic samples.

Identification of Photolysis Products in Acetonitrile from **2**

A product was isolated with a silica gel column chromatography, m/z 270 (M^+; 100), 242 (30), 214 (10), 188 (5), 167 (5), 149 (10), 135 (15), 121 (15), 107 (10), etc. ^{13}C NMR ($CDCl_3$; Me_4Si) δ = 161.2, 151.1, 144.9,, 138.8, 136.6, 135.0, 128.3, 127.7, 126.4, 125.2, 124.9, 124.4, 123.9, 121.7, 120.7, 117.6, 117.4, 116.3. ^1H NMR ($CDCl_3$; Me_4Si) δ = 9.12 (1H, d, 4.2), 9.09 (1H, d, 7.5), 9.01 (1H, d, 8.8), 8.50 (1H, d, 9.4), 8.34 (1H, d, 8.2), 8.00 (1H, d, 8.8), 7.95 (1H, d, 9.4), 7.77 (1H, d, 7.6), 7.66 (1H, dd, 7.5, 7.6), 7.54 (1H, dd, 4.2, 8.3). The product was assigned to fura[2,3-f:4,5-f']diquinoline (**10**).

Measurement of Quantum Yield of Fluorescence Spectra

The relative fluorescence quantum yields to that of quinine sulfate (ϕ = 0.55, 1.0×10^{-4} M in 1 N H_2SO_4) at 298 K were determined.[10]

Quenching Experiment of Fluorescence by Oxygen

Six 3-cm^3 solutions of **1** or **2** (1.0×10^{-4} M) were charged in six separate quartz cells (10 mm × 10 mm). Argon, air, 40, 60, 80% oxygen/nitrogen or pure oxygen gas was bubbled into the solutions until saturating at 20°C for 10 min, respectively. Concentration of oxygen in these solutions were evaluated from their solubilities in the solvent. Their emission spectra were recorded on a fluorescence spectrometer.

Measurement of Reaction Quantum Yields

The quantum yields of formation of products were measured as follows: A 3-cm^3 solvent solution of the substrate (1.0×10^{-3} M) saturated with argon gas in a quartz cell (10 mm × 10 mm) was irradiated using a low-pressure mercury lamp. Photoylsis was stopped within 10% conversion. Actinometry was carried out by use of a potassium trioxalatoferrate(III) solution.[11] The conversion of the substrate was determined by HPLC with using naphthalene as a standard.

Quenching Experiment of Quantum Yield of the Consumption of **2** *with Oxygen*

Six 3-cm^3 solutions of **2** (1.0×10^{-3} M) saturated with the prescribed concentration of oxygen were prepared, respectively, and their quantum yields were measured in the similar manner as described above.

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