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Photochemical P–O bond fission of aryl diethyl phosphates by a resonant two-photon reaction

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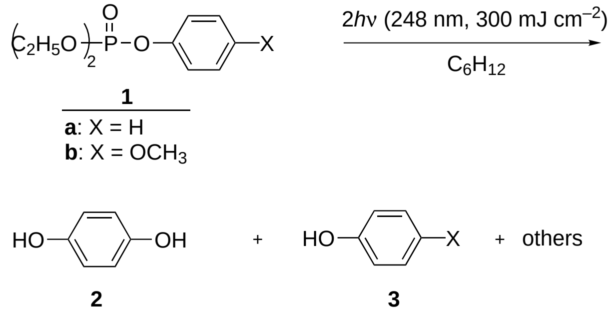
Abstract—Photochemical P–OAr bond fission of aryl diethyl phosphates was achieved via a resonant two-photon reaction using a KrF excimer laser, which gave 1,4-dihydroquinone and phenol derivatives. © 2001 Elsevier Science Ltd. All rights reserved.

A variety of one-photon reactions of phosphate esters have been reported from the mechanistic and synthetic viewpoints.[1] We have reported that the photoreaction of 4-methoxyphenyl phosphate in methanol occurs to produce anisole and free phosphate.[2] Obviously, O–Ar bond fission is the main process in one-photon reactions of aryl phosphates. It may be possible to observe other types of bond fission such as P–OAr bond fission from higher excited aryl phosphates with two-photon excitation, although two-photon reactions of aryl phosphates have not been reported.

It is known that the higher excited molecules generated with two-photon excitation undergo different reactions such as ionization and bond fission than the reaction of the lowest excited molecules. In addition to mechanistic studies, some synthetic applications of two-photon reactions of organic compounds have recently been reported due to improvements in laser equipment giving a high enough intensity for two-photon excitation.[3]

We report here that P–OAr bond homolysis of aryl diethyl phosphate **1** occurs to form $^{\bullet}$OAr radicals via a resonant two-photon process with a high-intensity excitation at 248 nm by a KrF excimer laser, contrary to the one-photon process where O–Ar bond fission occurs. Recently, a lot of attention has been paid to such $^{\bullet}$OAr radicals and residues ($(RO)_2(O)P^{\bullet}$) as intermediates in the actions of antioxidants and polymerization initiators, respectively.[4]

The one-pulse KrF excimer laser irradiation (100–300 mJ cm^{-2}) of **1** in aerated cyclohexane (5.0×10^{-4} M) produced 1,4-dihydroquinone **2**, phenol derivative **3**, and side products including trace amounts of benzene and anisole (Scheme 1).[†,‡] The conversion of **1**, chemi-



Scheme 1.

Keywords: resonant two-photon reaction; aryl diethyl phosphate; P–O bond fission; KrF excimer laser.

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[†] A 50 mm^3 sample solution (5.0×10^{-4} M) was placed in a quartz cell with a 10 mm width and 1 mm optical path. The fluence of the KrF excimer laser was controlled by means of a quartz convex lens. One pulse of the excimer laser irradiated the whole of the sample solution. The pulse energy was measured by means of a joulemeter and an oscilloscope. The pulse width (fwhm) of the excimer laser was 23 ns. The consumption of **1** and the yields of **2** and **3** were analyzed by HPLC in comparison with authentic compounds. The absorption maximums of **1a** and **1b** appeared at 262 nm (absorption coefficient: 408 mol^{-1} dm^3 cm^{-1}) and 279 nm (2060 mol^{-1} dm^3 cm^{-1}), respectively. The absorption coefficients of **1a** and **1b** at the excitation wavelength (248 nm) were 91 and 163 mol^{-1} dm^3 cm^{-1}, respectively.

[‡] The side products were unidentified except for benzene and anisole, which formed via one-photon processes of **1a** and **1b**. Since the one-photon products were yielded in trace amounts under the present experimental conditions, we did not quantitatively analyze the yields with various laser fluences.

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Table 1. Conversion (*C*) of **1**, chemical yields of the products based on **1** (*Y*), and based on consumed **1**[a]

	C (%)	*Y* (%)	
		2	**3**
1a[b]	6.5	4.3 (72)	0.31 (4.7)
1a[c]	1.2	0.63 (53)	0.058 (4.8)
1a[d]	5.7	4.7 (82)	0.13 (2.2)
1b[b]	14.9	5.7 (38)	3.2 (22)
1b[c]	3.7	1.4 (37)	0.56 (15)
1b[d]	7.8	6.3 (81)	1.1 (14)

[a] The yields of the products based on consumed **1** are parenthesized.

[b] Irradiated with 300 mJ cm^{-2} of the laser fluence in aerated cyclohexane.

[c] Irradiated with 100 mJ cm^{-2} of the laser fluence in aerated cyclohexane.

[d] Irradiated with 300 mJ cm^{-2} of the laser fluence in O_2 saturated cyclohexane.

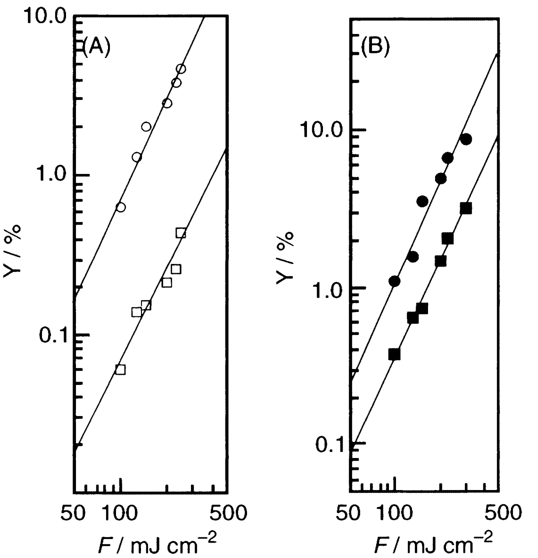
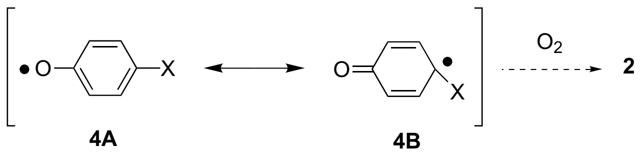
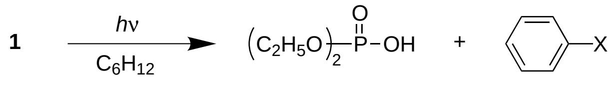


Figure 1. Correlation between product yields (*Y*) and laser fluence (*F*) on the laser irradiation of **1a** (A: open circle (**2**), open square (**3a**)) and **1b** (B: closed circle (**2**), closed square (**3b**)).



Scheme 2.



Scheme 3.

cal yields of the products based on **1** (*Y*) and based on consumed **1** are shown in Table 1. The laser irradiation of **1** in oxygen saturated cyclohexane raised the yield of **2** based on consumed **1** and suppressed the yield of **3** based on consumed **1** compared with the laser irradiation in aerated cyclohexane (Table 1).

Fig. 1 shows the yields of **2** and **3** as a function of laser fluence (*F*) for **1** in aerated cyclohexane. As can be seen in Fig. 1, *Y* increased with increasing *F*; the double-logarithmic plot between *Y* and *F* shows a linear correlation. The slopes were 2.06 and 1.82 for **2** and **3a**, respectively, on the laser irradiation of **1a** (Fig. 1A). A similar result was obtained in the KrF laser photolysis of **1b**; the slope was 2.20 for **2** and 2.01 for **3b** (Fig. 1B).[§] These results indicate that **2** and **3** were formed through the two-photon absorption of **1**.

The formation of the two-photon products **2** and **3** indicates that the initial photochemical process of **1** was P–OAr bond cleavage, which gave an $(EtO)_2(O)P^{\bullet}$ radical and an $^{\bullet}$OAr radical that were probably generated from **1** in a higher excited state. The generated $^{\bullet}$OAr radical (**4A**) likely abstracted a hydrogen atom from the cyclohexane to give **3**. The formation of **2** indicates the presence of a quinoid structure (**4B**) for the $^{\bullet}$OAr radical with the radical center at the 4-carbon (cf. Scheme 2). This is supported by the fact that a PM3 calculation of the $^{\bullet}$OAr radical showed high spin densities at the O and 4-C atoms. The spin densities at the O and 4-C atoms of the phenoxy radical were 0.168 and 0.338, and those of the 4-methoxyphenoxy radical were 0.146 and 0.318, respectively. The calculated spin densities of the phenoxy radical are qualitatively in agreement with values reported by another group.[5] The final product **2** was probably generated from the peroxy radicals formed by the reaction of **4B** with dissolved molecular oxygen, followed by successive hydrogen abstraction, O–O bond cleavage, and aromatization. This mechanism was supported by the results of the laser irradiation of **1** in oxygen-saturated cyclohexane.

The result of the KrF excimer laser photolysis of **1** was different from that of the conventional photolysis. Some benzene derivative and diethyl phosphate formed from the conventional photoirradiation in aerated cyclohexane; O–Ar bond dissociation occurred via a one-photon reaction (Scheme 3).[¶]

The two-photon excitation of **1** involved the first resonant π–π* excitation of the aryl group and the second excitation from the excited state (S_1, T_1, or CT state) to a higher excited **1** within a laser pulse (fwhm: 23 ns). We performed a laser flash photolysis of **1** to observe transient radicals. However, we did not observe any transient absorption in the wavelength region of 300–800 nm. This was probably due to the low absorption coefficients of the $(EtO)_2(O)P^{\bullet}$ and $^{\bullet}$OAr radicals. The chemical trapping of such radicals is now under way.

[§] The filter effect of the products was negligible in the present system. This was because the absorption coefficients of the products at 248 nm were not higher than those of **1** and the double logarithmic plots between *Y* and *F* were linear in the range of 100–300 mJ cm^{-2}.

[¶] A 5 dm^3 cyclohexane solution of **1** (1.0×10^{-3} M) was placed in a quartz tube of 10 mm diameter and irradiated using a 350 W high-pressure mercury lamp with water cooling.

In summary, we observed the first case of P–OAr bond splitting of **1** by the resonant two-photon reaction of **1**, where **2** and **3** formed from **1** in a higher excited state.

Acknowledgements

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