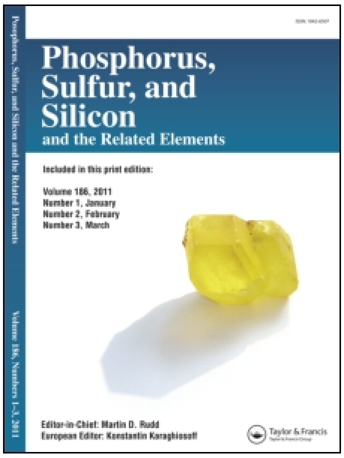

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PHOTOSUBSTITUTION OF METHOXYPHENYL PHOSPHATES

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PHOTOSUBSTITUTION OF METHOXYPHENYL PHOSPHATES

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Photosubstitution of diethyl methoxyphenyl phosphate with some nucleophiles (Cl^-, Br^-, CN^-) in methanol gave the corresponding 4-chloro-, 4-bromo-, and 4-cyanomethoxybenzenes through a singlet excited state. In acidic media, the reaction was accelerated. Upon further irradiation, halo-substituted methoxybenene underwent dehalogenation to give methoxybenzene. Methoxybenzene also formed directly through the homolytic PO-Ar bond cleavage. The order of reactivities of the isomers of the phosphate was 4- > 2- > 3-methoxyphenyl derivatives.

Key words: Photosubstitution; methoxyphenyl phosphate; chloromethoxybenzene; fluorescence.

INTRODUCTION

Although numerous examples of photochemical aromatic substitution reactions are known,[1-3] there are few reports concerning photosubstitution of aryl phosphate. Photosolvolysis of nitrophenyl phosphates was first observed and was studied extensively by de Jongh and Havinga.[4] The methanolysis of 3-nitrophenyl phosphate in alkaline media gave methyl phosphate and 3-nitrophenolate. This result indicates that methanol attack at the phosphorus atom has taken place. However photoreaction of 3-nitrophenyl phosphate with methylamine gave *N*-methyl-3-nitroaniline, in which the substitution occurred at the ring carbon atom.[3]

Tris(4-methoxyphenyl) phosphate gave overwhelmingly 4,4'-dimethoxybiphenyl through an intramolecular excimer upon UV-irradiation.[5]

It was reported that photocyanation of 4-chloromethoxybenzene or 1,4-dimethoxybenzene with cyanide ion in aqueous *t*-BuOH gave 1-cyanomethoxybenzene.[6]

In the present paper, photosubstitution of methoxyphenyl phosphates by some nucleophiles is reported.

RESULTS AND DISCUSSION

Photolysis of 4-Methoxyphenyl Phosphate (**1**) *in CH_3OH in the Presence of HCl*

Upon UV-irradiation of a methanol solution of **1** (2.0×10^{-2} mol dm^{-3}) in the presence of HCl (1.0 mol dm^{-3}), 4-chloromethoxybenzene (**2a**) was obtained as a primary product, but upon further irradiation, **2a** gradually decreased and methoxybenzene (**3**) increased. After an exhaustive irradiation, **2a** diminished and only **3** remained as shown in Figure 1.

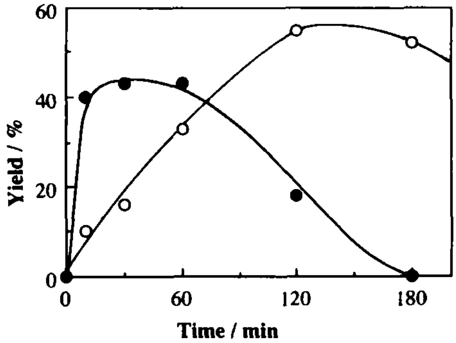
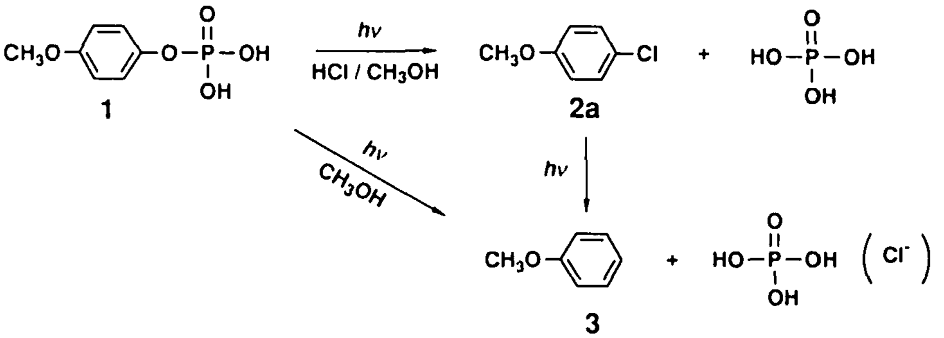


FIGURE 1 Product yields as a function of irradiation time. ●: **2a**, ○: **3**.

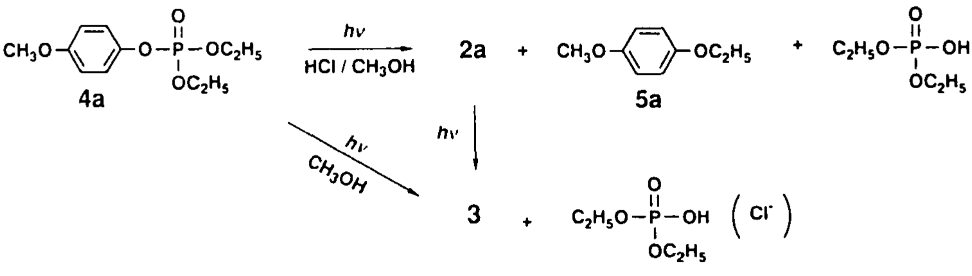


SCHEME I

Therefore, compound **3** may be a secondary product formed by photo-dechlorination of **2a**. Without HCl, the phosphate **1** was also photo-decomposed slowly to give **3** in a yield of 14% after 2 h-irradiation. Two paths can be assumed as the formation process of **3**; one is a dechlorination of **2a**, and another is a direct dephosphorylation of **1** by homolytic PO-Aryl bond cleavage (Scheme I).

Photolysis of Diethyl 4-methoxyphenyl Phosphate (**4a**) *in CH_3OH in the Presence of HCl*

Upon irradiation of a methanol solution of **4a** (2.0×10^{-2} mol dm^{-3}) in the presence of HCl (1.0 mol dm^{-3}) for 1 h (conv 60%), **2a** (23%), **3**, (23%), and 1,4-dimethoxybenzene (**5a**, 4%) were given. At the conditions without HCl, **4a** gave **3** (60%) and **5a** (15%) upon irradiation for 4 h (conv 95%).



SCHEME II

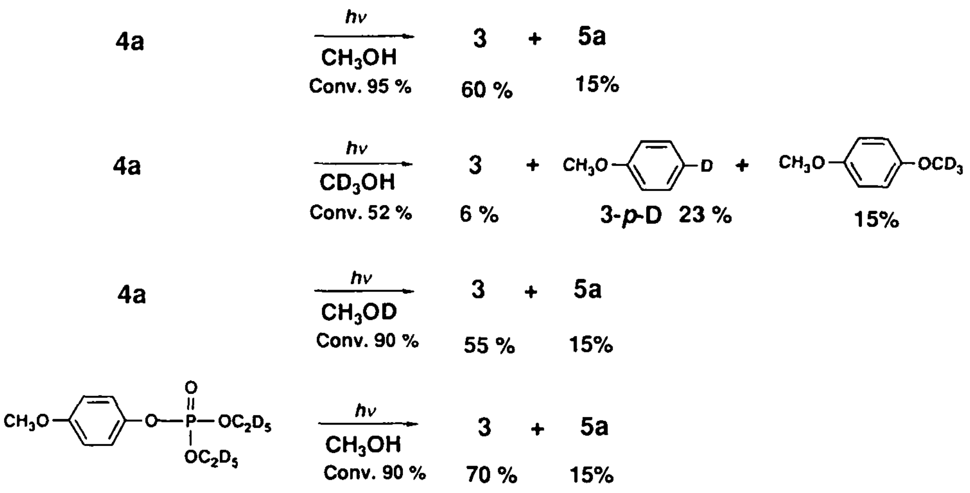
*Photolysis of **4a** in CH_3OH, CH_3OD, or CD_3OH Without HCl*

When **4a** was irradiated in CH_3OH, CH_3OD, or CD_3OH (2.0×10^{-2} mol dm^{-3}), respectively, products **3** and **5a** were also obtained. By product analysis with a mass spectrometer, it was found that deuterium was not contained in the product in CH_3OD as similar as in CH_3OH. In CD_3OH, **3**-*p*-D was obtained in a yield of 23% together with **3** in a yield of 6%. These results indicated that the formation of **3** may proceed through a homolytic PO-Aryl bond cleavage and the resulting methoxyphenyl radical may abstract a hydrogen of methyl of CH_3OH to give methoxybenzene. Photolysis of diethyl(C_2D_5) 4-methoxyphenyl phosphate gave only **3** and **5a** without **3**-*p*-D. This fact indicates that hydrogen abstraction by the radical did not occur intramolecularly.

Product **5a** may be derived from **4a** by direct photosubstitution with CH_3OH.

*Photolysis of Other Isomeric **4**; Diethyl 2-Methoxyphenyl Phosphate (**4b**) and 3-Methoxyphenyl Phosphate (**4c**) in CH_3OH in the Presence of HCl*

Upon UV-irradiation of the solution of **4a–c** (1.0×10^2 mmol dm^{-3}, HCl 0.1 mol dm^{-3}) for 4 h, the corresponding products of **2a–c**, **3**, and **5a–c**, were obtained. The results are summarized in Table I.



SCHEME III

TABLE I

Product yields in photolysis of the isomer of 4[a]

Substrate	Convn./%	Product yield/%		
		2	**3**	**5**
4a	60	23(**2a**)	23	4(**5a**)
4b	10	4(**2b**)	0	3(**5b**)
4c	25	14(**2c**)	6	2(**5c**)

a) Substrate (2.0×10^{-2} mol dm^{-3}) and HCl (0.1 mol dm^{-3}) irradiated for 30 min.

The order of the reactivities of the isomers was **4a** > **4c** > **4b**. It can be concluded that a rule which plays a major role in determining position in this substitution is ortho/para orientation with regard to the methoxy groups.

Photosubstitution of **4a** *with Other Nucleophiles in CH_3OH*

Photosubstitution with other nucleophiles in CH_3OH was carried out, and the product yields and quantum yields are summarized in Table II.

The substitution product **2** could not be obtained with diethylamine and KF, but in these cases **3** and **5a** were formed in the same yield as in other cases.

Kinetic Study

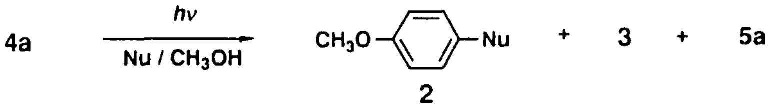
Fluorescence spectrum of **2a** is shown in Figure 2. The emission maxima was 310 nm. The fluorescence was quenched with KCl as shown in the figure. A linear correlation between the concentration of KCl and the intensity of fluorescence (I_f) was found (Stern-Volmer analysis, Scheme IV, Equation (1)).

$$I_f^0/I_f = 1 + kq\tau[\mathrm{KCl}] \qquad (1)$$

$$k_q = k_1 + k_2$$

$$k_D = k_d + k_e + k_r$$

$$\tau = 1/(k_d + k_e + k_r)$$



FORMULA I

TABLE II

Quantum yield, product yield, and $kq\tau$ in photolysis of **4a** in the nucleophiles in MeOH

Nucleophiles	$kq\tau$[a)]	ϕ of **2**[b)]	Yield of products/%[c)]		
Nu	mol dm^{-3}		**2**	**3**	**5a**
$(C_3H_7)_2NH$	-	-	0(0)	25(56)	9(20)
KF	36	-	0(0)	27(56)	11(21)
KCl	51	0.042	17(0)	21(60)	5(12)
HCl	58	0.058	23(0)	23(64)	4(3)
KBr	53	0.044	9(0)	26(94)	0(4)
KCN	71	0.011	11(30)	0(0)	0(0)

a) *kq* is a quenching rate constant, and τ is a lifetime of singlet excited state of **4a**. Detail was described in the text.

b) The quantum yield of **2** was determined under the conversion 10%. Detail procedure was described in experimental section.

c) The yields were determined by GLC after 30 min irradiation, respectively. The yields in parentheses indicated the yields after 3 h irradiation.

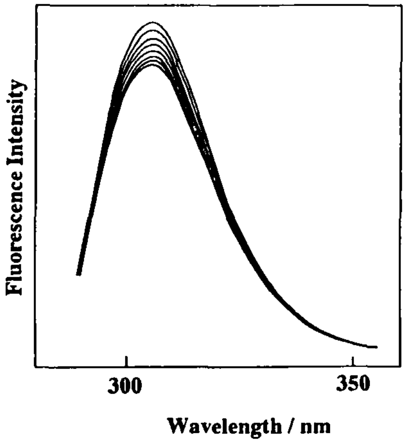
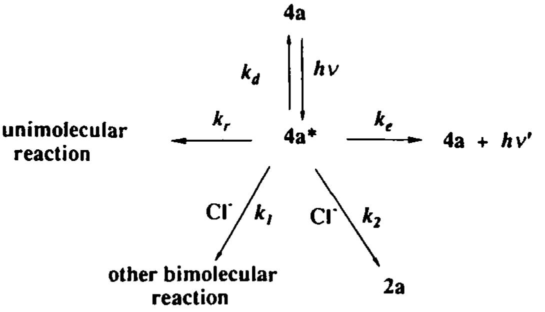


FIGURE 2 Quenching experiment of fluorescence of **4a** by KCl. Concentration; **4a**; 0.1 × 10^{-3} mol dm^{-3}. KCl; in MeOH, 0.00, 0.49, 0.96, 1.40, 1.83, 2.24, 2.69, 2.99 × 10^{-3} mol dm^{-3} in order from top, λ_{ex} = 280 nm.



SCHEME IV

From the slope of the line $k_q\tau$ was obtained, where k_q is the rate constant of the reaction of photo-excited intermediate with chloride and τ is the lifetime of the intermediate; k_D is the rate constant for the inherent rate of unimolecular deactivation of **4a***. Other nucleophiles, KF, KBr and KCN also quenched the fluorescence in a similar manner. These $k_q\tau$ values are given in Table II. These results indicated that the order of rate constants of the intermediate with the nucleophile was KCN < KBr < KCl < KF.

The yield of **2a** was increased with an increase of the amount of KCl. A linear relationship existed between the reciprocal of the quantum yield ϕ and the reciprocal of the concentration of KCl (Stern-Volmer analysis, Equation 2).[7]

$$\begin{aligned} \phi &= \alpha k_2[\mathrm{KCl}]/(k_q[\mathrm{KCl}] + k_D) \\ 1/\phi &= (k_q[\mathrm{KCl}] + k_D)/\alpha k_2[\mathrm{KCl}] \\ &= 1/\alpha(k_q/k_2 + k_D/k_2[\mathrm{KCl}]) \qquad (2) \end{aligned}$$

A plot of $1/\phi$ versus $1/[\mathrm{KCl}]$ is predicted by Equation (2) to yield a straight line with slope equal to $s = kD/\alpha k_2$ and the intercept of $i = k_q/(\alpha k_2)$.

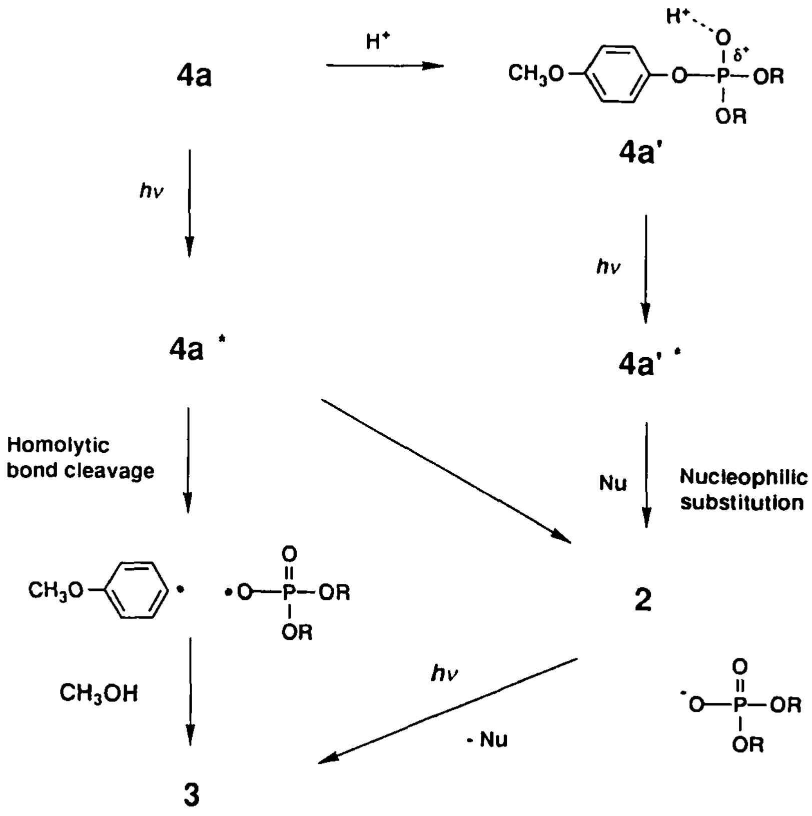
$$i/s = (k_q/\alpha k_2)(\alpha k_2/k_D) = k_q/k_D = k_q\tau$$

Where α is efficiency of formation of **4a***, k_2 is the rate constant for bimolecular reaction, and k_q is the rate constant for all biomolecular quenching. The $k_q\tau$ value was 47 mol dm^{-3}, which agreed closely with that obtained by fluorescence quenching of **4a** with KCl. The result suggested that formation of **2a** proceeds through a singlet excited state.

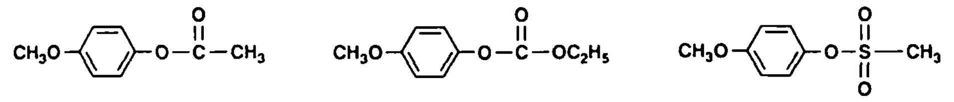
The yield of **2a** was greater in HCl than in KCl solution; substitution of chloride was facilitated in acidic media. The effect could be understood by the assumption that the increase of positive charge on the phosphorus atom (quasi-phosphonium ion) by proton attack to phosphoryl oxygen (having the highest negative charge) may facilitate the PO-Aryl bond cleavage.[8] Overall reaction scheme is shown in Scheme V.

Photolysis of Other 4-Methoxyphenolate

4-Methoxyphenyl acetate (**6**), ethoxycarbonate (**7**), and methylsulfonate (**8**) were irradiated in the similar manner. But these compounds were stable except **6**, which was partially isomerized to 2-acetylmethoxybenzene (photo-Fries rearrangement[9]).



SCHEME V


6 7 8

FORMULA II

EXPERIMENTAL

Material. 4-Methoxyphenyl phosphate (**1**); mp 93–95°C, λ_{max} (MeOH) 280 nm (ε 2200 mol^{-1} cm^2). Diethyl 4-methoxyphenyl phosphate (**4a**); bp 135–140°C/2.0 mmHg, λ_{max} (MeOH) 280 nm (ε 2200 mol^{-1} cm^2). Diethyl 3-methoxyphenyl phosphate (**4b**); bp 134–138°C/2.0 mmHg, λ_{max} (MeOH) 274 nm (3500), 278 (3000). Diethyl 2-methoxyphenyl phosphate (**4c**); bp 130–134°C/2.0 mmHg, λ_{max} (MeOH) 273 nm (2900), 280 (2600). 4-Methoxyphenyl acetate (**6**); bp 87–89°C/2 mmHg, mp 34–35°C, λ_{max} (MeOH) 275 nm (ε 7200 mol^{-1} cm^2). Ethyl 4-methoxyphenyl carbonate (**7**); bp 96–98°C/2 mmHg, λ_{max} (MeOH) 275 nm (ε 1800 mol^{-1} cm^2). Methoxyphenyl methylsulphonate (**8**); m.p. 80–81°C, λ_{max} (MeOH) 275 nm (ε 1500 mol^{-1} cm^2).

Hydrogen chloride/methanol solution was prepared by bubbling dried HCl gas into cooled methanol solution until saturation.

Photolysis. A 3 ml solution of substrate (10^{-2} mol dm^{-3}) was charged into a quartz tube (10 mm) with a nucleophile (10^{-1} mol dm^{-3}), and argon gas was bubbled into the solution for 10 min. The tube was sealed with a rubber septa (or a fixed amount of hydrogen chloride/methanol solution was injected with a micro syringe) and irradiated with a high pressure Hg lamp. At several minutes intervals, 0.1 ml samples were withdrawn with a syringe and analyzed with GLC directly. The products were assigned with the authentic samples prepared by the other methods.

Measurement of Quantum Yield. The quantum yields were measured as follows: A 3-ml methanol solution of the substrate (1.0×10^{-2} mol dm^{-3}) and nucleophile (1.0×10^{-1} mol dm^{-3}) saturated with argon gas containing nucleophile (3.0×10^{-2} mol dm^{-3}) in a quartz cell (10 mm × 10 mm) was irradiated using a low-pressure Hg lamp (60 W). Photolysis was carried out within 10% conversion. Actinometry was carried out by use of a potassium trioxalatoferrate (III) solution.[10] The product yields were determined by GLC using triphenylmethane as an internal standard.

Quenching Experiment of Fluorescence with KCl. Six 3-ml methanol solutions of **4a** (1.0×10^{-4} mol dm^{-3}) were charged in eight separate quartz cells (10 mm × 10 mm). Argon gas was bubbled into the solutions until saturating at 20°C for 10 min. Concentrations of KCl in these solutions were 0.00, 0.49, 0.96, 1.40, 1.83, 2.24, 2.69, 2.99 × 10^{-3} mol dm^{-3}, respectively. Their emission spectra were recorded on a fluorescence spectrometer.

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