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Photolysis of bis(methoxyphenyl) methylphosphonates

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Abstract

On UV irradiation in methanol, bis(methoxyphenyl) methylphosphonates undergo ipso coupling of two methoxyphenyl groups or intramolecular rearrangement of a methoxyphenyl group to give dimethoxybiphenyl and trimethoxybiphenyl respectively. They exhibit two emission bands attributed to a monomeric excited methoxyphenyl group and an intramolecular excimer. Their fluorescence spectra and reactivities are affected by the position of the methoxyl group on the benzene ring. The intramolecular excimer of bis(3-methoxyphenyl) methylphosphonate is more polar than that of bis(4-methoxyphenyl) methylphosphonate, because the former has a more unsymmetrical aryl group than the latter. Dimethoxybiphenyl may be formed through a non-polar intramolecular excimer, while trimethoxybiphenyl may be formed through a polar excimer or a monomeric excited state. The reactivities also depend on the position of the methoxyl group and decrease in the order 4->3->2-methoxyphenyl.

Keywords: Photolysis

1. Introduction

Generally, the formation of an intramolecular excimer requires the incorporation of two chromophores separated by a certain number of carbon atoms. For instance, in compounds of the type A–$(CH_2)_n$–A, the efficiency of intramolecular excimer formation is a function of n. Often for $n=3$ an optimum situation is obtained. This indicates that the formation of an intramolecular excimer is favoured when a steric situation is satisfied [1–6]. The photolysis of tris(4-methoxyphenyl) phosphate in methanol gives 4,4′-dimethoxybiphenyl and 4-methoxyphenyl phosphate [7,8]. It has also been reported that the photolysis of bis(4-methoxyphenyl) phosphate in acidic media involves the intramolecular ipso coupling of two 4-methoxyphenyl groups through a singlet intramolecular excimer to give 4,4′-dimethoxybiphenyl, whereas it does not react in basic media [9]. The fluorescence spectra of these phosphates exhibit two emission bands: a long-wavelength emission band due to an intramolecular excimer of two 4-methoxyphenyl groups and a short-wavelength emission band due to an excited 4-methoxyphenyl group (monomer).

In this paper, the effect of the position of the methoxyl group in the benzene ring on the reactivities and fluorescence spectra of bis(methoxyphenyl) methylphosphonates (**1a**–**1c**) and bis(dimethoxyphenyl) methylphosphonates (**2**, **3**) is discussed.

2. Results and discussion

On UV irradiation of methylphosphonates (**1a**–**1c**) in methanol, two kinds of product were obtained: trimethoxybiphenyl (**4a**–**4c**) and dimethoxybiphenyl (**5a**–**5c**). Gas–liquid chromatography (GLC) analysis, after treatment of the photolysed products with diazomethane, revealed the formation of dimethyl methylphosphonate (**6**) (Scheme I). The product yields of **4** and **5** and the quantum yields of **5** are summarized in Table 1.

The photochemical reactivities of **1** decreased in the following order: **1a** (*p*-)>**1b** (*m*-)>**1c** (*o*-), and the product ratio of **4**/**5** increased in the same order. On photolysis of **1a** in ethanol (conversion, 45%), **5a** (27%) and 2,5-diethoxy-4′-methoxybiphenyl (**4a′**) (9%) were obtained. Two ethoxyl groups in **4a′** may come from the solvent ethanol. On photolysis of **1b** in ethanol (conversion, 27%), **5b** (10%) and 2-ethoxy-4,3′-dimethoxybiphenyl (**4b′**) (9%) were obtained, in which only one methoxyl group was replaced with an ethoxyl group (Scheme II).

On UV irradiation of bis(3,5-dimethoxyphenyl) methylphosphonate (**2**) in methanol under the same con-

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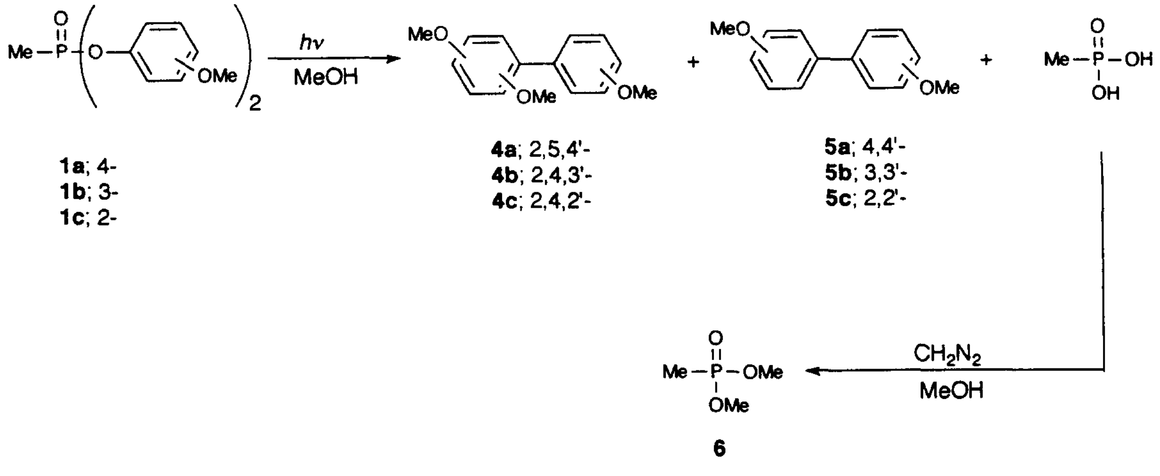
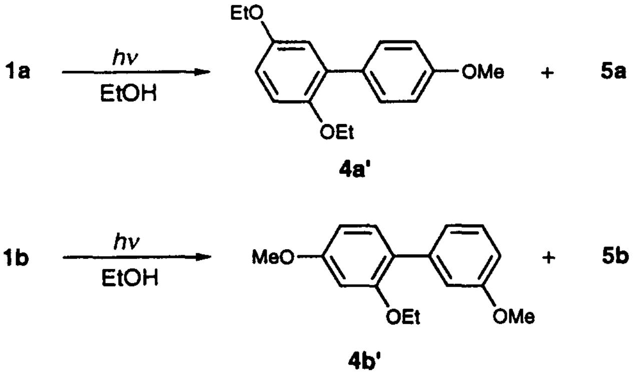


Scheme I.

Table 1
Photolysis of **1a–1c**[a]

Compound	Conversion (%)	Product yield (%)		Quantum yield of 5 $\phi(\times 10^2)$
		4	5	
1a	64	12	31	4.0
1b	34	11	12	2.3
1c	25	11	5	1.8

[a] **1a–1c** (10^{-2} M) in methanol, irradiated by a high-pressure Hg lamp (300 W) with a Vycor filter at ambient temperature under Ar for 1 h.



Scheme II.

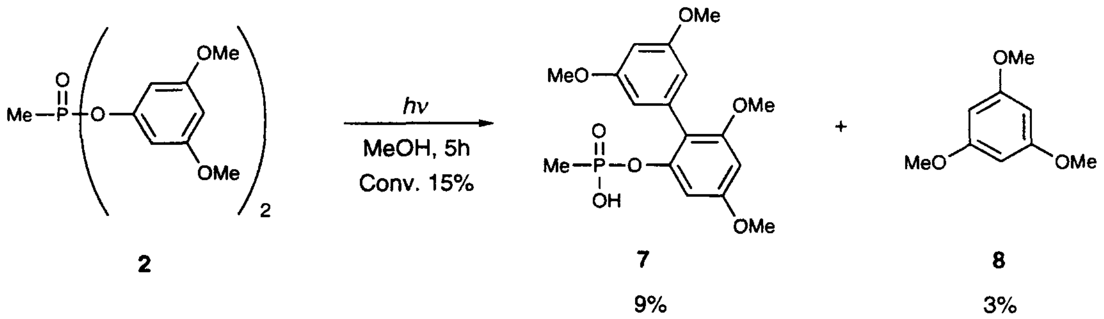
ditions for 5 h (conversion, 15%), 2-(3′,5′-dimethoxyphenyl)-3,5-dimethoxyphenyl methylphosphonate (**7**) and 1,3,5-trimethoxybenzene (**8**) were obtained in 9% and 3% yields respectively (Scheme III). Photolysis of bis(2,6-dimethoxyphenyl) methylphosphonate (**3**) (conversion, 6%) gave 2,6-dimethoxyphenol (**9**) (3%) and a trace amount of 1,2,3-trimethoxybenzene (**10**) by direct high performance liquid chromatography (HPLC) analysis (Scheme IV). For **2** and **3**, the product derived from intramolecular ipso coupling between two dimethoxyphenyl groups was not obtained, the two products originating from an intramolecular rearrangement of a dimethoxyphenyl group and/or photosolvolysis of **2** or **3** with methanol [10]. Their photochemical reactivities were lower than that of **1**.

The fluorescence spectra of **1a–1c**, **2** and **3** consisted of two emission bands: a long-wavelength emission band (350–370 nm) was attributed to an intramolecular excimer and a short-wavelength emission band (300–310 nm) was attributed to a singlet excited methoxyphenyl group (monomer). Fig. 1 shows the fluorescence spectra of these phosphonates. For the fluorescence spectrum of **1c**, it is not clear from the spectral shape whether the spectrum consists of two different emission bands. However, from quenching studies on the fluorescence spectrum by oxygen and measurement of the fluorescence lifetime by the single-photon-counting method, it was found that there were two components and their $k_q\tau$ and τ values were different.

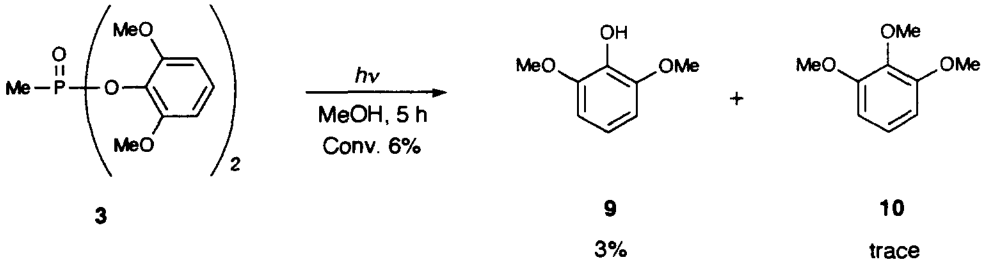
The maxima of the monomer and excimer emission bands of **1a** changed only slightly with a change in solvent (CH_3OH, tetrahydrofuran (THF), CH_3CN, etc.), whereas the maximum of the excimer emission band of **1b** shifted to longer wavelength and the relative intensities of the monomer and excimer emission bands decreased with increasing polarity of the solvent. A linear correlation between the frequencies of the emission maxima (ν_f) of **1b** and the solvent polarities derived from Eq. (1) was observed as shown in Figs. 2 and 3.

$$f(\epsilon, n) = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/2(2n^2 + 1) \qquad (1)$$

ϵ and n are the dielectric constant and the refractive index of the solvent respectively (Mataga–Lippert equation) [11–13]. These results suggest that there is no charge transfer interaction between the two 4-methoxybenzene rings of **1a**, whereas there is some charge transfer interaction between the two 3-methoxybenzene rings of **1b**. Therefore the intramolecular excimer of **1b** can be considered as an unsymmetric excimer or a type of exciplex. The dipole moment (μ_{ex}) of the



Scheme III.



Scheme IV.

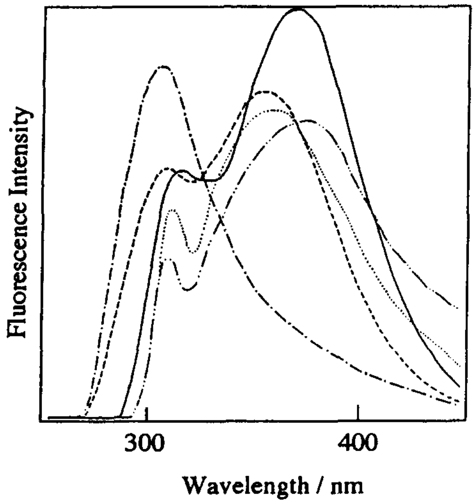


Fig. 1. Fluorescence spectra of **1a** (——), **1b** (– – –), **1c** (–·–), **2** (–··–) and **3** (·····) in methanol (10^{-4} M, $\lambda_{ex}=280$ nm).

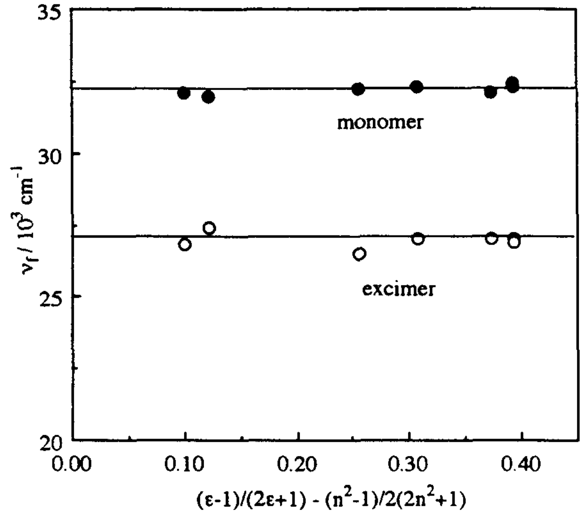


Fig. 2. Relationship between $(\epsilon-1)/(2\epsilon+1)-(n^2-1)/2(2n^2+1)$ of the solvent and ν_f of **1a**.

excimer of **1b** can be calculated from Eq. (2)

$$\nu_f = \epsilon^0 - (2\mu_{ex}^2/hcr^3)f(\epsilon, n) \qquad (2)$$

where h is Planck's constant, c is the velocity of light and r is the effective radius of the solvent cavity. The dipole moment (μ_{ex}) for **1b** was calculated as 2.1×10^{-29} Cm, assuming $r=470$ pm. It has been reported that intermolecular exciplexes between aromatics and cyano compounds have large polarities, and their dipole moments (μ_{ex}) have been estimated as $(3.3\text{–}5.0)\times10^{-29}$ Cm [14]. It has also been reported that a singlet intramolecular exciplex of 4-cyanophenyl-4-methoxyphenyl methylphosphonate has a dipole moment of 3.5×10^{-29} Cm [15].

The fluorescence spectra of **1a**–**1c**, **2** and **3** and the formation of **4a**–**4c** and **5a**–**5c** were quenched by dissolved oxygen. Stern–Volmer analysis of the quenching of the fluorescence spectra by oxygen showed that the monomer and excimer bands were quenched in different ways. The $k_q\tau$ values, lifetimes, quenching rate constants and fluorescence quantum yields of **1a**–**1c** are shown in Table 2.

Similar quenching studies on the quantum yields of **4a**–**4c** and **5a**–**5c** obtained on photolysis of **1a**–**1c** were performed. The results are summarized in Table 3.

The $k_q\tau$ values of the quenching of the formation of **4a** and **5a** were in close agreement with the $k_q\tau$

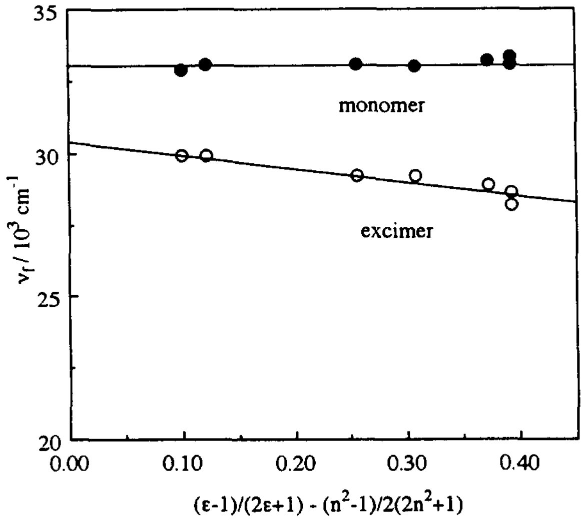


Fig. 3. Relationship between $(\epsilon-1)/(2\epsilon+1)-(n^2-1)/2(2n^2+1)$ of the solvent and ν_f of **1b**.

values of the fluorescence quenching of the monomer and excimer of **1a** respectively. In addition, the $k_q\tau$ values of the quenching of the formation of **5b** and **5c** were in approximate agreement with the $k_q\tau$ values of the fluorescence quenching of the excimer of **1b** and **1c** respectively. However, the Stern–Volmer plot for **4b** and **4c** was not linear. Therefore the formation of **4b** and **4c** probably proceeds through another process.

Quenching studies on products from **2** and **3** could not be performed because they were less reactive. Most of their excited species were thermally deactivated, and their fluorescence quantum yield was low.

From these results, it can be concluded that, for **1a**, the formation of **4a** may proceed via electrophilic attack of a singlet excited monomeric methoxyphenyl group on another group. The intermediate **11** may be in equilibrium with **13** by migration of a 4-methoxyphenyl group via a σ-bridged carbonium intermediate (**12**). The ethoxyl derivative **4a′** may be formed from **11** or **13** by nucleophilic substitution of ethanol. Product **5a** may be formed by intramolecular ipso coupling of two 4-methoxyphenyl groups in concert with O–C bond fissions through a non-polar singlet intramolecular excimer (Scheme V).

The phosphonate **1b** containing unsymmetrical methoxyphenyl groups may have a net dipole moment, and charge separation or polarization in the 3-methoxyphenyl group may be obtained in the excited state. The product **4b** may be produced by intramolecular electrophilic attack of the polarized group on the neighbouring group. The product **5b** may be formed via intramolecular ipso coupling of two aryl groups in a symmetric excimer. In the intermediate **14**, containing a 3-methoxyphenyl group, a σ-bridged cation (intermediate **12**) is not formed and 1,2-migration of a 3-methoxyphenyl group does not occur. Therefore, on photolysis of **1b** in ethanol, only a monoethoxyl derivative **4b′** is obtained (Scheme VI).

In the case of **1c**, the mechanism of formation of **4c** is not clear, whereas **5c** is obtained mainly through an intramolecular non-polar excimer.

In the case of the photolysis of 4-cyanophenyl-4-methoxyphenyl methylphosphonate, an intramolecular electrophilic attack of a 4-methoxyphenyl group on a cyanophenyl group occurs through an intramolecular exciplex to give 2(4′-methoxyphenyl)-4-cyanophenyl methylphosphonate; the formation of biaryl by ipso coupling is a minor process [15]. From these results, it is concluded that the ratio of the product obtained via electrophilic attack of the methoxyphenyl group to the product obtained via ipso coupling of the groups increases with an increase in the polarity of the singlet excited intramolecular complexes.

3. Experimental details

3.1. Apparatus

Melting points were obtained with a Yanagimoto micropoint apparatus. CHN microanalyses were ob-

Table 2

$k_q\tau$, lifetimes (τ)[a], quenching rate constants (k_q) and quantum yields (ϕ_f) of fluorescence[b] of **1a**–**1c**, **2** and **3** (10^{-4} M, in methanol, λ_{ex}=280 nm)

Compound	Monomer			Excimer			ϕ_f ($\times10^2$)
	$k_q\tau$ (M^{-1})	τ (ns)	k_q ($\times10^{10}$ M^{-1} s^{-1})	$k_q\tau$ (M^{-1})	τ (ns)	k_q ($\times10^{10}$ M^{-1} s^{-1})	
1a	41	0.99	4.1	111	6.25	1.8	4.0
1b	29	0.68	3.5	63	4.77	1.3	3.6
1c	14	1.07	1.3	67	5.27	1.3	2.7
2	45	–	–	71	–	–	0.4
3	40	–	–	66	–	–	0.5

[a] Fluorescence lifetimes at 298 K were measured by the time-correlated, single-photon-counting method.

[b] Fluorescence quantum yields at 298 K were determined relative to that of quinine sulphate (10^{-4} M) in 1 N sulphuric acid (ϕ=0.55) [16].

Table 3
$k_q\tau$ of formation of products

Compound	$k_q\tau$ (M^{-1})	
	4	5
a	58	100
b	[a]	76
c	[a]	111

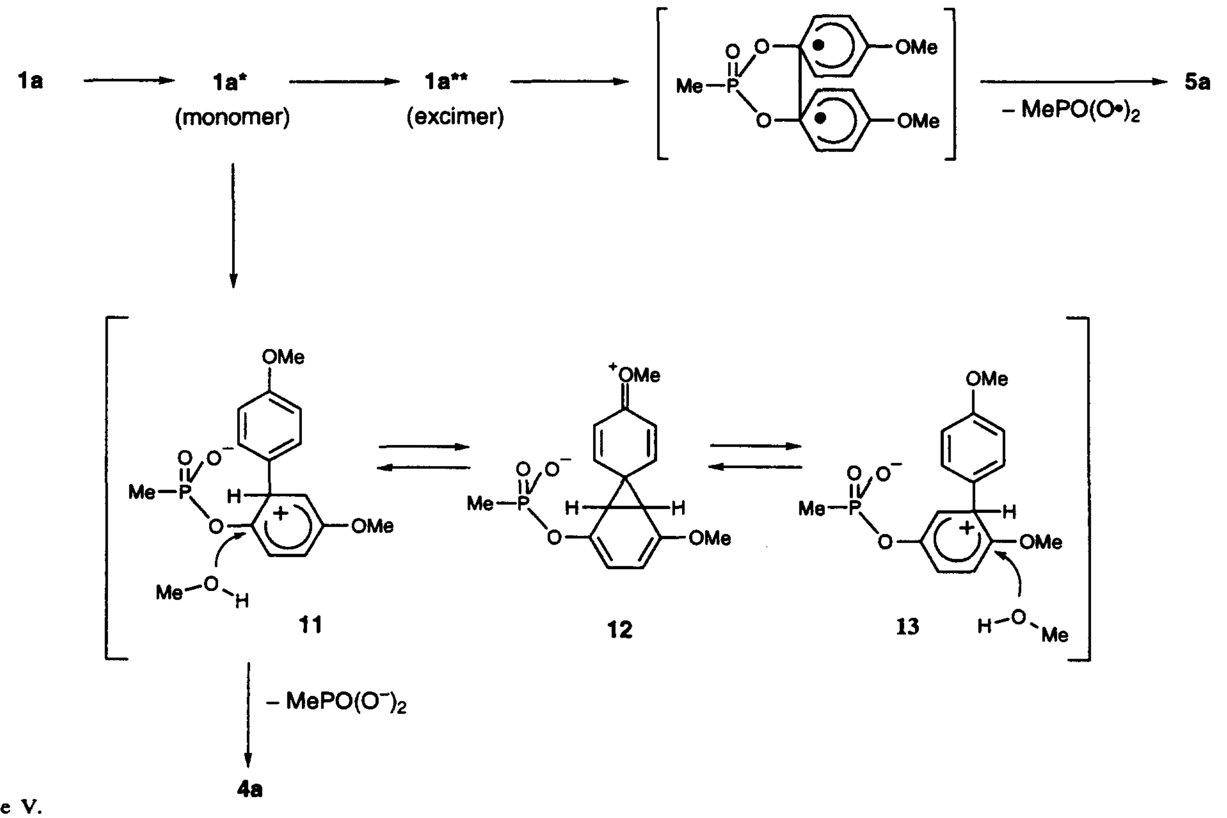
[a] In these cases, the Stern–Volmer plots were not linear. Therefore $k_q\tau$ was not determined.

tained with a Perkin–Elmer model 240 analyser. UV–visible spectra were recorded with a Hitachi 150-20 spectrometer. Steady state fluorescence spectra were recorded with a Hitachi 850 fluorescence spectrometer. Fluorescence lifetimes were measured by the time-correlated, single-photon-counting method using a Horiba NAES-1100 time-resolved fluorescence spectrometer. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were determined in $CDCl_3$ with tetramethylsilane as internal standard on a Bruker-AM600 spectrometer. ^{31}P NMR spectra were determined in $CDCl_3$ with 80% H_3PO_4 as external standard on a JEOL FX 90Q spectrometer. GLC analyses were carried out using 2% Silicone OV-17 on Chrom WAW DMCS (60–80 mesh). Gas chromatography–mass spectrometry (GC–MS) was performed using a JMS-DX 300, and high-resolution mass spectra were obtained on a JMS-01SG-2 instrument. HPLC analyses were carried out using a Shimadzu LC-10AS instrument with a column of Shiseido CAPCELL PAK C18 AG 120. Photolysis was carried out using a 250 ml doughnut-type quartz cell (outer diameter, 60 mm; inner diameter, 40 mm; height, 170 mm). A 300 W high-pressure mercury lamp EHBW-300 (Eikosha Co., Ltd.) equipped with a water cooling jacket was used. Quantum yields of the products were obtained using a quartz cell (10 mm × 10 mm) with a 60 W low-pressure mercury lamp ELJ-60 (Eikosha Co., Ltd.).

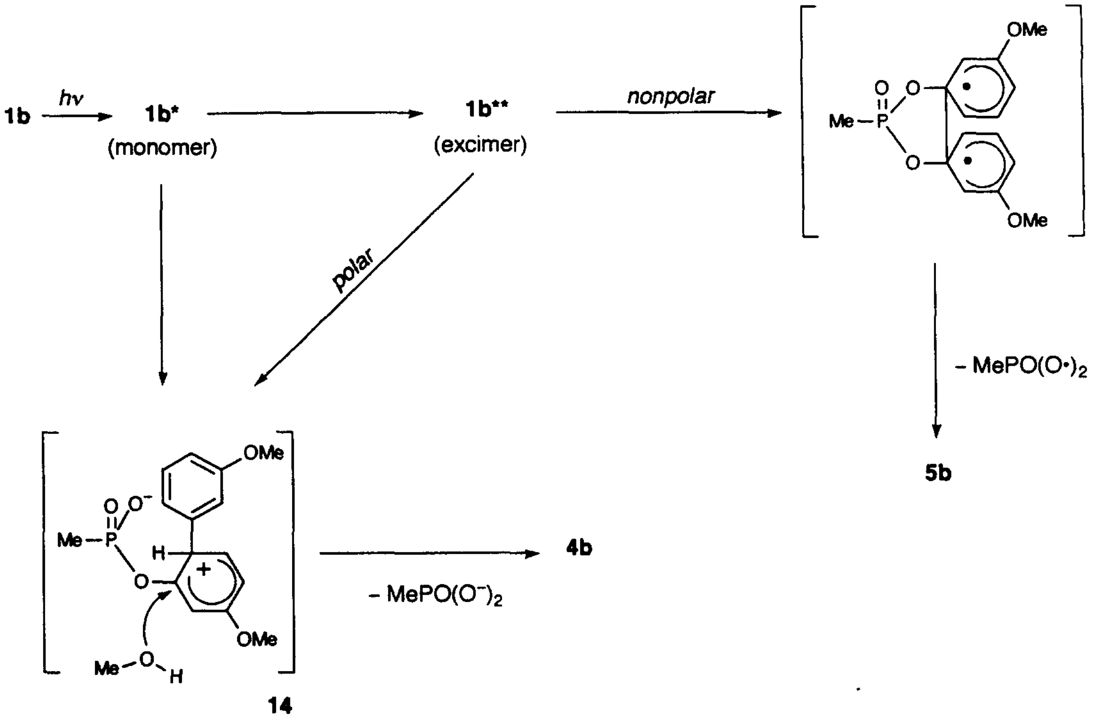
3.2. Materials

Bis(4-methoxyphenyl) methylphosphonate (1a)

An equivalent molar mixture of 4-methoxyphenol and triethylamine in ether was added dropwise to an ether solution of methylphosphonyl dichloride (0.5 M). After workup, the crude product was chromatographed on silica gel (eluent, chloroform–hexane (1 : 3)) to give a pure product as a colourless oil [2]. Boiling point (b.p.), 171–172 °C (0.2 mmHg). Found: C, 58.21%; H, 5.49%; P, 10.35%. $C_{15}H_{17}O_5P$ requires: C, 58.44%; H, 5.56%; P, 10.05%. λ_{max} (MeOH) (nm) 278 (ϵ (M^{-1} cm^{-1}) 4680). ^1H NMR ($CDCl_3$; Me_4Si) δ 1.80 (3H, d, J_{HP} 17.6, Me), 3.79 (6H, s, OMe), 7.34 (8H, m, Ar). ^{31}P NMR ($CDCl_3$; 80% H_3PO_4) δ 25.0 (q, J_{PH} 17.1).



Scheme V.



Scheme VI.

Bis(3-methoxyphenyl) methylphosphonate (1b)

Compound **1b** was prepared by the reaction of methylphosphonyl dichloride with 3-methoxyphenol in a similar manner to that described above. B.p., 164–166 °C (0.2 mmHg). Found: C, 58.40%; H, 5.59%; P, 10.17%. $C_{15}H_{17}O_5P$ requires: C, 58.44%; H, 5.56%; P, 10.05%. λ_{max} (MeOH) (nm) 271 (ϵ (M^{-1} cm^{-1}) 3480). ^{1}H NMR ($CDCl_3$; Me_4Si) δ 1.78 (3H, d, J_{HP} 17.8, Me), 3.76 (6H, s, OMe), 6.73 (1H, d, J 7.9, Ar), 6.75 (1H, s, Ar), 6.83 (1H, d, J 7.9, Ar), 7.22 (1H, t, J 7.9, Ar). ^{31}P NMR ($CDCl_3$; 80% H_3PO_4) δ 25.0 (q, J_{PH} 17.8).

Bis(2-methoxyphenyl) methylphosphonate (1c)

Compound **1c** was prepared by the reaction of methylphosphonyl dichloride with 2-methoxyphenol in a similar manner to that described above. Melting point (m.p.), 59–60 °C. Found: C, 58.29%; H, 5.49%; P, 10.11%. $C_{15}H_{17}O_5P$ requires: C, 58.44%; H, 5.56%; P, 10.05%. λ_{max} (MeOH) (nm) 270 (ϵ (M^{-1} cm^{-1}) 5420). ^{1}H NMR ($CDCl_3$; Me_4Si) δ 1.89 (3H, d, J_{HP} 18.5, Me), 3.85 (6H, s, OMe), 6.89 (1H, d, J 6.9, Ar) 6.95 (1H, d, J 7.9, Ar), 7.12 (1H, dd, J 6.9, 7.9, Ar), 7.19 (1H, dd, J 6.9, 7.9, Ar). ^{31}P NMR ($CDCl_3$; 80% H_3PO_4) δ 25.0 (q, J_{PH} 18.1).

Bis(3,5-methoxyphenyl) methylphosphonate (2)

Compound **2** was prepared by the reaction of methylphosphonyl dichloride with 3,5-dimethoxyphenol in a similar manner to that described above. B.p., 196–198 °C (0.2 mmHg). Found: C, 55.27%; H, 5.59%; P, 8.11%. $C_{17}H_{21}O_7P$ requires: C, 55.44%; H, 5.75%; P, 8.41%. λ_{max} (MeOH) (nm) 269 (ϵ (M^{-1} cm^{-1}) 2050). ^{1}H NMR ($CDCl_3$; Me_4Si) δ 1.78 (3H, d, J_{HP} 17.8, Me), 3.74 (12H, s, OMe), 6.29 (2H, s, Ar), 6.39 (4H, s, Ar). ^{31}P NMR ($CDCl_3$; 80% H_3PO_4) δ 25.0 (q, J_{PH} 18.1).

Bis(2,6-methoxyphenyl) methylphosphonate (3)

Compound **3** was prepared by the reaction of methylphosphonyl dichloride with 2,6-methoxyphenol in a similar manner to that described above. M.p., 90–91 °C. Found: C, 55.25%; H, 5.49%; P, 8.27%. $C_{17}H_{21}O_7P$ requires: C, 55.44%; H, 5.75%; P, 8.41%. λ_{max} (MeOH) (nm) 268 (ϵ (M^{-1} cm^{-1}) 1690). ^{1}H NMR ($CDCl_3$; Me_4Si) δ 2.00 (3H, d, J_{HP} 18.8, Me), 3.79 (12H, s, OMe), 6.57 (4H, d, J 8.5, Ar), 7.02 (2H, t, J 8.5, Ar). ^{31}P NMR ($CDCl_3$; 80% H_3PO_4) δ 25.0 (q, J_{PH} 18.1).

3.3. Preparation of authentic samples

Trialkoxybiphenyl (4a–4c, 4a′ and 4b′)

The compounds **4a–4c**, **4a′** and **4b′** were prepared by anisylation of dialkoxybenzene. The reactions were carried out with monoalkoxybenzenediazonium borofluorides and dialkoxybenzenes at a molar ratio of 1:30 at 230 °C for 4 h [17]. They were purified by column chromatography (silica gel; eluent, benzene). Their GC–MS and ^{1}H and ^{13}C NMR data agree with those of the products isolated from photolysis.

4,4′-Dimethoxybiphenyl (5a)

The compound **5a** was prepared by methylation of 4,4′-dihydroxybiphenyl with dimethyl sulphate in an alkaline aqueous solution. M.p., 201–202 °C. Found: C, 78.55%; H, 6.61%. $C_{14}H_{14}O_2$ requires: C, 78.48%; H, 6.59%.

2,2′-Dimethoxybiphenyl (5c)

The compound **5c** was prepared by methylation of 2,2′-dihydroxybiphenyl with dimethyl sulphate in an alkaline aqueous solution. M.p., 155–156 °C. Found: C, 78.55%; H, 6.61%. $C_{14}H_{14}O_2$ requires: C, 78.48%; H, 6.59%.

The GC–MS and ^{1}H and ^{13}C NMR data agree with those of the products isolated from photolysis.

3.4. Photolysis

General photolysis procedure

Methanol or ethanol solutions (200 ml) of **1a–1c**, **2** and **3** (10^{-2} M) were charged in doughnut-type quartz cells with argon bubbling to purge off dissolved air. After irradiation with a 300 W high- pressure mercury lamp (with water cooling (20–25 °C)) for 1 h, the reaction mixtures were, directly or after methylation with diazomethane, analysed by HPLC, GLC or GC–MS and compared with authentic samples prepared as described above. The product yields were determined by HPLC and GLC using biphenyl as standard. In some cases, the reaction products were isolated by column chromatography (silica gel) and identified by ^{1}H and ^{13}C NMR spectroscopy.

3.5. Product analysis

Photolysis of bis(4-methoxyphenyl) methylphosphonate (1a)

The photolysis products of **1a** were analysed by GC–MS after methylation with diazomethane. 4,4′-Dimethoxybiphenyl (**5a**) and dimethyl methylphosphonate (**6**) were confirmed by comparison with the GC retention times and mass spectra of authentic samples prepared by the methods described above. 2,5,4′-Trimethoxybiphenyl (**4a**) and 2,5-diethoxy-4′-methoxybiphenyl (**4a′**) were isolated by column chromatography (silica gel; eluent, benzene). **4a**: ^{1}H NMR ($CDCl_3$; Me_4Si) δ 3.84 (3H, s, OMe), 3.80 (3H, s, OMe), 3.75 (3H, s, OMe), 6.81 (1H, d, *J* 11.0, Ar), 6.89 (1H, s), 6.90 (1H, d, *J* 11.0, Ar), 6.96 (2H, d, *J* 9.3, Ar), 7.47 (2H, d, *J* 9.3, Ar); ^{13}C NMR ($CDCl_3$; Me_4Si) δ 55.2, 55.6, 56.3, 112.5, 112.6, 113.5, 116.5, 130.4, 130.7, 131.3, 150.7, 153.7, 158.7. **4a′**: ^{1}H NMR ($CDCl_3$; Me_4Si) δ 1.21 (3H, t, *J* 6.9, OEt), 1.32 (3H, t, *J* 6.9, OEt), 3.76 (3H, s, OMe), 3.84 (2H, q, *J* 6.9, OEt), 3.93 (2H, q, *J* 6.9, OEt), 6.70 (1H, d, *J* 8.9, Ar), 6.81 (1H, d, *J* 8.9, Ar), 6.82 (1H, s), 6.86 (2H, d, *J* 8.9, Ar), 7.43 (2H, d, *J* 8.9, Ar); ^{13}C NMR ($CDCl_3$; Me_4Si) δ 14.9, 55.2, 64.0, 65.1, 113.4, 114.8, 114.9, 117.1, 131.0, 131.8, 150.0, 153.2, 158.6. These data agreed with those of authentic samples.

Photolysis of bis(3-methoxyphenyl) methylphosphonate (1b)

The photolysis products of **1b** were analysed in the same manner to that described above. 2,4,3′-Trimethoxybiphenyl (**4b**) and 2-ethoxy-4,3′-dimethoxybiphenyl (**4b′**) were isolated by column chromatography (silica gel; eluent, benzene). **4b**: ^{1}H NMR ($CDCl_3$; Me_4Si) δ 3.79 (3H, s, OMe), 3.82 (3H, s, OMe), 3.84 (3H, s, OMe), 6.55 (1H, s, Ar), 6.56 (1H, d, *J* 8.9, Ar), 6.84 (1H, d, *J* 7.9, Ar), 7.06 (1H, s, Ar), 7.08 (1H, d, *J* 8.0, Ar), 7.24 (1H, d, *J* 8.9, Ar), 7.29 (1H, dd, *J* 7.9, 8.0, Ar); ^{13}C NMR ($CDCl_3$; Me_4Si) δ 55.2, 55.4, 55.5, 99.0, 104.6, 112.0, 115.3, 122.0, 128.8, 123.4, 131.2, 139.7, 157.4, 159.8, 160.4. **4b′**: ^{1}H NMR ($CDCl_3$; Me_4Si) δ 1.24 (3H, t, *J* 6.9, OEt), 3.75 (3H, s, OMe), 3.78 (3H, s, OMe), 3.93 (2H, q, *J* 6.9, OEt), 6.56 (1H, s, Ar), 6.59 (1H, d, *J* 8.9, Ar), 6.80 (1H, d, *J* 7.6, Ar), 6.99 (1H, s, Ar), 7.08 (1H, d, *J* 7.9, Ar), 7.17 (1H, d, *J* 8.9, Ar), 7.23 (1H, dd, *J* 7.6, 7.9, Ar); ^{13}C NMR ($CDCl_3$; Me_4Si) δ 14.8, 55.4, 55.5, 64.9, 99.3, 105.1, 112.4, 115.5, 121.8, 123.3, 129.0, 131.2, 139.1, 158.8, 159.8, 160.6. These data agreed with those of authentic samples.

Photolysis of bis(2-methoxyphenyl) methylphosphonate (1c)

The photolysis products of **1c** were analysed in the same manner to that described above. 2,4,2′-Trimethoxybiphenyl (**4c**) was isolated by column chromatography (silica gel; eluent, benzene). ^{1}H NMR ($CDCl_3$; Me_4Si) δ 3.73 (3H, s, OMe), 3.80 (3H, s, OMe), 3.84 (3H, s, OMe), 6.52 (1H, d, *J* 8.0, Ar), 6.54 (1H, s, Ar), 6.94 (1H, d, *J* 7.9, Ar), 6.96 (1H, dd, *J* 7.3, 7.9, Ar), 7.15 (1H, d, *J* 8.0, Ar), 7.22 (1H, d, *J* 7.3, Ar), 7.28 (1H, dd, *J* 7.2, 7.9); ^{13}C NMR ($CDCl_3$; Me_4Si) δ 55.2, 55.5, 55.7, 98.8, 104.1, 111.0, 120.2, 120.3, 127.5, 128.2, 131.5, 131.6, 157.1, 157.9, 160.1. These data agreed with those of authentic samples.

Photolysis of bis(3,5-dimethoxyphenyl) methylphosphonate (2)

The photolysis products of **2** were analysed directly by HPLC. 1,3,5-Trimethoxybenzene (**8**) was confirmed by comparison of the HPLC retention time with that of an authentic sample which was commercially available. 3,5-Dimethoxy-2-(3,5-dimethoxyphenyl)phenyl methylphosphonate (**7**) was isolated by column chromatography (silica gel; eluent, benzene–THF (6 : 4)). ^{1}H NMR ($CDCl_3$; Me_4Si) δ 1.06 (3H, d, J_{HP} 17.4, Me), 1.92 (1H, s, OH), 3.74 (3H, s, OMe), 3.75 (3H, s, OMe), 3.76 (3H, s, OMe), 3.77 (3H, s, OMe), 6.28 (1H, s, Ar), 6.38 (1H, s, Ar), 6.42 (1H, s, Ar), 6.48 (2H, s, Ar).

Photolysis of bis(2,6-dimethoxyphenyl) methylphosphonate (3)

The photolysis products of **3** were analysed directly by HPLC; 2,6-dimethoxyphenol (**9**) and 1,2,3-trimethoxybenzene (**10**) were confirmed by comparison of the HPLC retention times with those of authentic samples which were commercially available.

3.6. Measurement of quantum yield

The quantum yields of product formation were measured as follows. A methanol solution (3 ml) of the substrate (1.0×10^{-2} M) saturated with argon gas in a quartz cell (10 mm×10 mm) was irradiated using a low-pressure Hg lamp (60 W). Photolysis was carried out with 10% conversion. Actinometry was performed using potassium trioxalatoferrate(III) solution [18]. The product yield was determined by GLC using biphenyl as standard.

The fluorescence quantum yields at 298 K were determined relative to that of quinine sulphate (1.0×10^{-4} M) in 1 N sulphuric acid ($\phi = 0.55$) as reference [8].

3.7. Quenching of fluorescence by oxygen

Six methanol solutions (3 ml) of the substrate (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 was bubbled into the solutions until saturation at 20 °C for 10 min. The concentrations of oxygen in these solutions were evaluated from their solubilities in methanol to be 0.0, 1.51, 3.82, 5.72, 7.63 and 9.54×10^{-3} M respectively. Their emission spectra were recorded on a fluorescence spectrometer.

The $k_q\tau$ values were determined from the Stern–Volmer equations (Eqs. (3) and (4)). In these cases, it was assumed that the monomer and excimer are not in equilibrium. For the monomer

$$\phi_m^0/\phi_m = 1 + k_{qm}\tau_m[O_2] \quad (3)$$

For the excimer

$$(\phi_e^0/\phi_e)/(\phi_m^0/\phi_m) = 1 + k_{qe}\tau_e[O_2] \quad (4)$$

where ϕ is the quantum yield of fluorescence, k_q is the quenching rate constant and τ is the fluorescence lifetime.

3.8. Quenching of quantum yield of product by oxygen

Six methanol solutions (3 ml) of the substrate (1.0×10^{-2} M) saturated with the concentrations of oxygen given above were prepared. Their quantum yields were measured in a similar manner to that described above. The values were determined by the following equations. For **4**

$$\phi_4^0/\phi_4 = 1 + k_{q4}\tau_4[O_2] \quad (5)$$

For **5**

$$(\phi_5^0/\phi_5)/(\phi_4^0/\phi_4) = 1 + k_{q5}\tau_5[O_2] \quad (6)$$

where ϕ is the quantum yield of formation of products, k_q is the quenching rate constant and τ is the lifetime. For the calculation of $k_{q5}\tau_5$ in Eq. (6), ϕ_m^0/ϕ_m in Eq. (4) was used instead of ϕ_4^0/ϕ_4.

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