

## Photolysis of 4-Methoxyphenyl Aryl Alkylphosphonates

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UV irradiation of bis(4-methoxyphenyl) methylphosphonate **1a** in methanol gave 4,4'-dimethoxybiphenyl **2a** as the main product through an intramolecular excimer. With 4-cyanophenyl-4-methoxyphenyl methylphosphonate **1b** 4-cyano-4'-methoxybiphenyl **2c** and 4-cyano-2-(4'-methoxyphenyl)phenyl methylphosphonate **4b** were obtained through an intramolecular exciplex. 3-Cyanophenyl-4-methoxyphenyl methylphosphonate **1c** gave only 3-cyano-4'-methoxybiphenyl **2f**. Methyl 4-methoxyphenyl 4-chlorobenzylphosphonate **5a** gave methyl 4-chlorobenzyl-2-(4'-methoxyphenyl)phosphonate and methyl 2-(4'-methoxyphenyl)benzylphosphonate.

Emission of an intermolecular excimer generally formed by an electronically excited molecule and an unexcited molecule has been observed for a number of aromatic hydrocarbons. Intramolecular excimer formation was inferred upon incorporation of two chromophores into a single molecule separated by a particular number of carbon atoms; *i.e.*, in compounds of type A-[CH<sub>2</sub>]<sub>n</sub>-A (A = chromophore), the efficiency of formation of an intramolecular excimer is a function of *n* and often was optimal when *n* = 3.<sup>1-3</sup> This result indicates that intramolecular excimer formation is favoured when a particular steric situation is satisfied. In the course of our studies on the photolysis of bis(4-methoxyphenyl) methylphosphonate and tris(4-methoxyphenyl) phosphate, it has been found that they have intramolecular excimer emission bands, which correlate closely with their photo-reactivities.<sup>4-6</sup> In this paper, we describe the photochemical behaviour of some diaryl methylphosphonates and aryl arylmethylphosphonates, in which two chromophores are connected by O-P-O or O-P-CH<sub>2</sub>. The reaction mechanism will also be discussed.

### Results and Discussion

#### Reaction Products

**Photolysis of Diaryl Methylphosphonate 1.**—UV irradiation of bis(4-methoxyphenyl) methylphosphonate **1a** in methanol (10<sup>-2</sup> mol dm<sup>-3</sup>) under an argon atmosphere with a high-pressure mercury lamp for 1 h (conversion 73%) gave 4,4'-dimethoxybiphenyl **2a** (yield 69%, quantum yield  $\phi$  = 0.12) and 2,5,4'-trimethoxybiphenyl **2b** (trace) and treatment of this photolysed product with diazomethane led to dimethyl methylphosphonate **3b** (68%).

Photolysis of 4-cyanophenyl 4-methoxyphenyl methylphosphonate **1b**, which has two different aryl groups, under similar

conditions (conv'n. 26%), gave 4-cyano-4'-methoxybiphenyl **2c** (2%) and a trace of 5-cyano-2-hydroxy-4'-methoxybiphenyl **2d** (direct GLC analysis). After treatment with diazomethane the mixture was shown by analysis to contain methyl 4-cyano-2-(4'-methoxyphenyl)phenyl methylphosphonate **4b** (11%,  $\phi$  = 0.049), **3b** (2%) and a trace of 5-cyano-2,4'-dimethoxybiphenyl **2e**. Hydrolysis of the photolysed mixture with aqueous sodium hydroxide increased the amount of **2d** considerably (12%). Methylation of the hydrolysed product gave **2e** (11%).

Upon irradiation of 3-cyanophenyl-4-methoxyphenyl methylphosphonate **1c**, under the same conditions (conv'n. 5%), only 3-cyano-4'-methoxybiphenyl **2f** was obtained (2%,  $\phi$  = 0.044). The dimethyl ester **3b** (4%) was also detected after treatment with diazomethane.

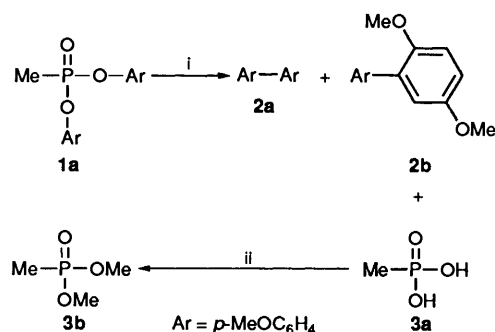
Photolysis of 4-chlorophenyl-4-methoxyphenyl methylphosphonate **1d** under the same conditions (conv'n. 59%), followed by treatment with diazomethane gave 4-chloro-4'-methoxybiphenyl **2g** (5%), methyl 4-chloro-2-(4'-methoxyphenyl)phenyl methylphosphonate **4c** (29%,  $\phi$  = 0.088), and **3b** (4%).

**Photolysis of Aryl Arylmethylphosphonate 5.**—UV irradiation of a methanol solution of 4-methoxyphenylmethyl 4-chlorobenzylphosphonate **5a** under the same conditions (conv'n. 87%), followed by treatment with diazomethane, gave dimethyl 4-chloro-2-(4'-methoxyphenyl)benzylphosphonate **6a** (70%,  $\phi$  = 0.14) and dimethyl 2-(4'-methoxyphenyl)benzylphosphonate **6b** (5%), which is derived from photo-dechlorination of **6a** (detected by a direct GC-analysis).

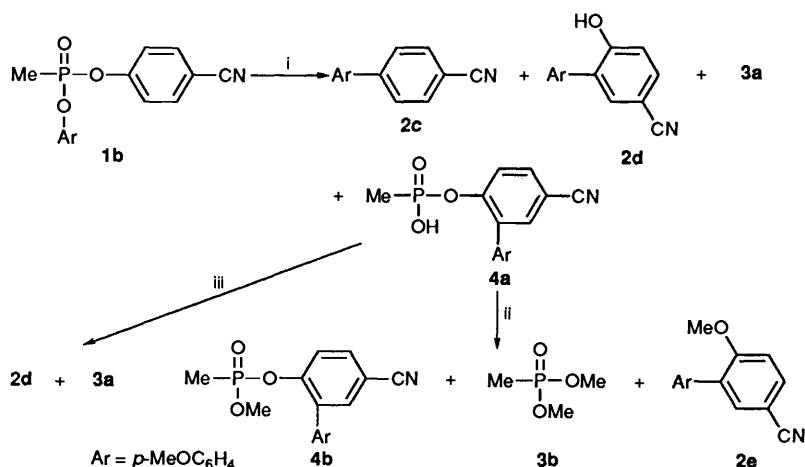
Bis(4-methoxyphenyl) 4-chlorobenzylphosphonate **5b** (conv'n. 84%) gave **2a** (30%), **2b** (3%), dimethyl 4-chlorobenzylphosphonate **3d** (20%), methyl 4-methoxyphenyl 4-chloro-2-(4'-methoxyphenyl)benzylphosphonate **6c** (16%), and methyl 4-methoxyphenyl 2-(4'-methoxyphenyl)benzylphosphonate **6d** (1.0%) after treatment with diazomethane. The phosphonate **6d** might be derived from further photolysis of **6c**.

4-Chlorophenyl methyl 4-methoxybenzylphosphonate failed to react under similar conditions.

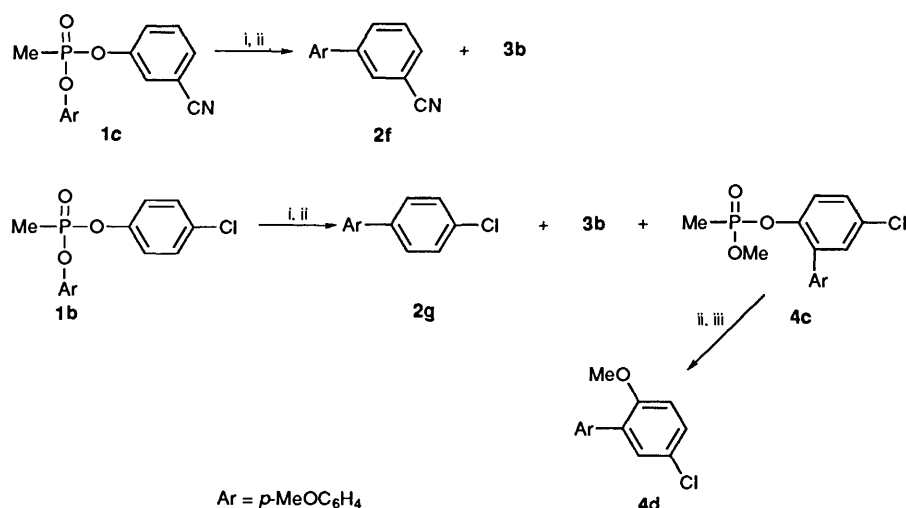
**Fluorescence Spectra.**—The fluorescence spectra of **1a-d** and **5a** in acetonitrile are shown in Fig. 1. These spectra consists of two emission bands, respectively. The relative intensities of the two bands were substantially independent of the substrate concentration (10<sup>-4</sup>–10<sup>-6</sup> mol dm<sup>-3</sup>). Further studies on the behaviour of these fluorescence spectra established that they had characteristics associated with an excited monomer and intramolecular excimer or exciplex emission bands as described by Hirayama.<sup>1</sup> Therefore, the longer wavelength emission band was ascribed to the intramolecular excimer or exciplex and the shorter band to the excited monomer, respectively.



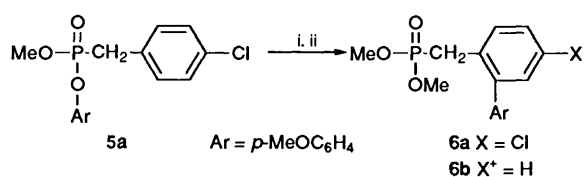
Scheme 1 Reagents and conditions: i, *hν*, MeOH; ii, CH<sub>2</sub>N<sub>2</sub>, MeOH



**Scheme 2** Reagents and conditions: i,  $h\nu$ , MeOH; ii, 5% NaOH, aq. EtOH, reflux; iii,  $\text{CH}_2\text{N}_2$ , MeOH



**Scheme 3** Reagents and conditions: i,  $h\nu$ , MeOH; ii,  $\text{CH}_2\text{N}_2$ , MeOH; iii, 5% NaOH, aq. EtOH, reflux



**Scheme 4** Reagents and conditions: i,  $h\nu$ , MeOH; ii,  $\text{CH}_2\text{N}_2$ , MeOH

**Solvent Effect.**—Although the maxima and intensities of the excimer emission bands of **1a** were scarcely affected by the solvent (MeOH, THF, MeCN, etc.), in contrast, with increasing solvent polarity, the exciplex emission bands of **1b** and **1c** were shifted to longer wavelength and the relative intensities of monomer and exciplex emission bands were reduced. A linear correlation between frequency of the exciplex emission maxima ( $\nu_c$ ) of **1b** in the solvent and the solvent polarity derived from eqn. (1), was obtained (see Fig. 2).

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

where  $\epsilon$  and  $n$  are the dielectric constant and the refractive index for solvent, respectively (Mataga-Lippert equation).<sup>7</sup> This result confirmed the formation of an exciplex, the dipole moment of which ( $\mu_{\text{ex}}$ ) was calculated from the slope for eqn. (2):

$$\nu_c = \epsilon_0 - (2\mu_{\text{ex}}^2/hcr^3) f(\epsilon, n) \quad (2)$$

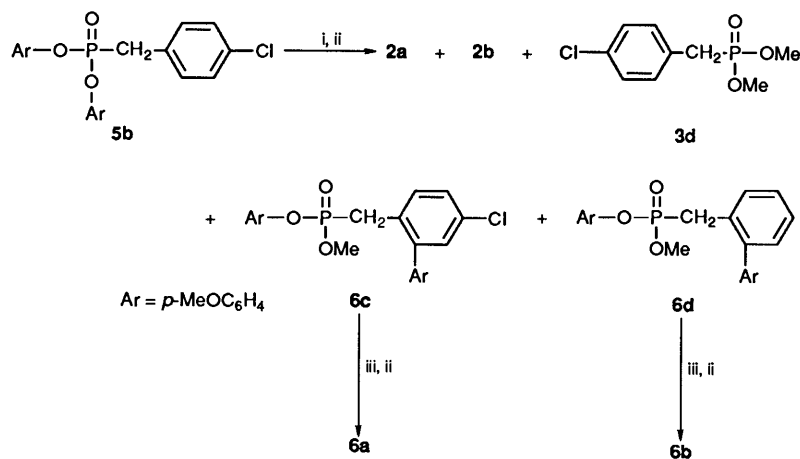
where  $h$  is Planck's constant,  $c$  is the velocity of light, and  $r$  is the effective radius of the solvent cavity. The dipole moment  $\mu_{\text{ex}}$  was calculated as  $3.5 \times 10^{-29}$  Cm for **1b**, assuming  $r$  as 300 pm.

In the case of **1c**, a linear correlation between the frequency of exciplex emission and the solvent polarities was also observed, a value of  $1.9 \times 10^{-29}$  Cm being obtained for  $\mu_{\text{ex}}$ .

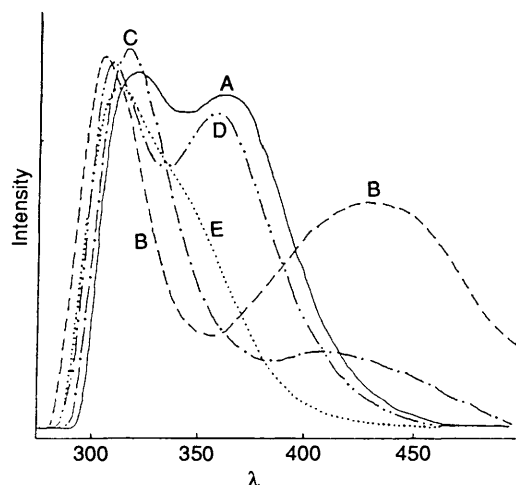
The emission spectra of **1d**, **5a** and **5b** were unaffected by the polarity of the solvent. These results suggest that there is no charge-transfer interaction between a methoxybenzene ring and a chlorobenzene ring, a result dissimilar to that for methoxybenzene and cyanobenzene.

However, in the case of **5a**, a rough correlation between the yield of **6a** and the acceptor number, which expresses the acceptor property of solvent,<sup>9</sup> was obtained (Fig. 3). The electrophilic solvent increased the yield of **6a**, an effect which may be understood by assuming that the increase of positive charge on the phosphorus atom (quasi-phosphonium ion) by electrophilic attack of solvent on the phosphoryl oxygen may facilitate O-Ar bond cleavage.<sup>8</sup> Addition of acetic acid to the solution (MeCN) of **5a** also increased the yield of **6a**.

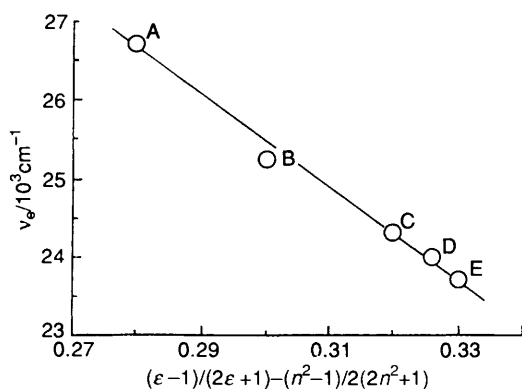
A similar correlation was also observed between the chemical shift of the phosphorus and the yield of **6a**.



**Scheme 5** Reagents and conditions: i, *hν* 1 h, MeOH; ii, CH<sub>2</sub>N<sub>2</sub> MeOH; iii, 5% NaOH, aq. EtOH, reflux

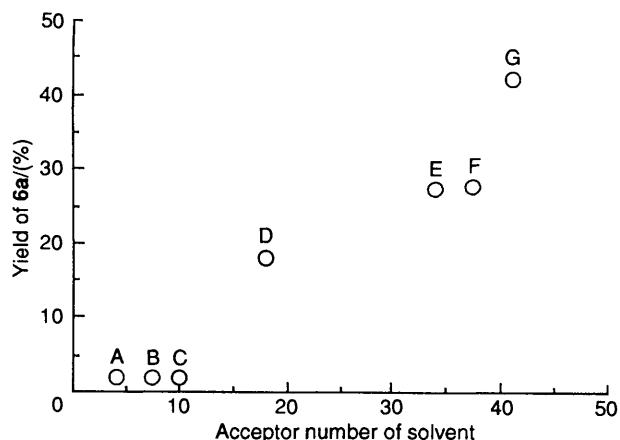


**Fig. 1** Fluorescence spectra of **1a** (A), **1b** (B), **1c** (C), **1d** (D), and **5a** (E) in MeCN ( $10^{-4}$  mol dm<sup>-3</sup>,  $\lambda_{\text{ex}}$  280 nm)



**Fig. 2** Correlation between the polarity parameter of the solvent,  $(\epsilon - 1)/(2\epsilon - 1) - (n^2 - 1)/2(2n^2 + 1)$ , and  $\nu_e/\text{cm}^{-1}$  of **1b**. A = Et<sub>2</sub>O, B = THF; C = Bu<sup>t</sup>OH, D = Pr<sup>i</sup>OH, E = EtOH

**Quenching Experiment with Oxygen.**—It was found that the fluorescence of **1b** and formation of **4b** were quenched with oxygen. The fluorescence quenching with oxygen showed that monomer and exciplex bands were quenched in different manners. Thus, different  $k_q\tau$  values were obtained when the simple Stern–Volmer equation was applied to monomer and exciplex fluorescence. This result implies that monomer and exciplex are not in equilibrium. For this case,  $k_{\text{qm}}\tau_{\text{m}}$  and



**Fig. 3** Correlation between acceptor number of the solvent and yield of **6a**. A = Et<sub>2</sub>O, B = THF, C = 1,4-dioxane, D = MeCN, E = Pr<sup>i</sup>OH, F = EtOH, G = MeOH.

$k_{\text{qe}}\tau_{\text{e}}$  can be evaluated by eqns. (3) and (4), where  $k_{\text{qm}}$  and  $k_{\text{qe}}$  are oxygen quenching rate constants for monomer and exciplex, and  $\tau_{\text{m}}$  and  $\tau_{\text{e}}$  are the lifetimes of the fluorescence of monomer and exciplex, respectively.

$$\varphi_{\text{m}}^{\circ}/\varphi_{\text{m}} = (1 + k_{\text{qm}}\tau_{\text{m}}[Q]) \quad (3)$$

$$\varphi_{\text{e}}^{\circ}/\varphi_{\text{e}} = (1 + k_{\text{qm}}\tau_{\text{m}}[Q])(1 + k_{\text{qe}}\tau_{\text{e}}[Q]) \quad (4)$$

therefore,

$$(\varphi_{\text{e}}^{\circ}/\varphi_{\text{e}})(\varphi_{\text{m}}^{\circ}/\varphi_{\text{m}}) = 1 + k_{\text{qe}}\tau_{\text{e}}[Q] \quad (5)$$

For monomer band (320 nm)  $k_{\text{qm}}\tau_{\text{m}} = 51$  mol<sup>-1</sup> dm<sup>3</sup> (correlation coefficient:  $r = 0.999$ ) was obtained, while for exciplex band (380 nm)  $k_{\text{qe}}\tau_{\text{e}} = 110$  mol<sup>-1</sup> dm<sup>3</sup> ( $r = 0.973$ ) was obtained.

A similar quenching experiment for quantum yield of **4b** from **1b** was performed, and as the result,  $k_{\text{q1}}\tau_1 = 135$  mol<sup>-1</sup> dm<sup>3</sup> ( $r = 0.990$ ) was obtained, where  $k_{\text{q1}}$  and  $\tau_1$  are an oxygen quenching rate constant and a lifetime for the active species giving **4b**, respectively. This value agreed nearly with the  $k_{\text{qe}}\tau_{\text{e}}$  value obtained from the fluorescence quenching experiment. Therefore, the formation of **4b** probably proceeds through a singlet excited intramolecular exciplex.

A similar fluorescence quenching experiment of **5a** with oxygen gave  $k_{\text{qm}}\tau_{\text{m}} = 11$  mol<sup>-1</sup> dm<sup>3</sup> ( $r = 0.999$ ) for monomer



triethylamine. After work-up, the crude product was chromatographed on silica gel (eluent: chloroform-hexane, 1:3) to give the pure title compound as colourless oil (Found: C, 58.2; H, 5.5; P, 10.35.  $C_{15}H_{17}O_5P$  requires C, 58.44; H, 5.56; P, 10.05%);  $\lambda_{\max}(\text{MeOH})/\text{nm}$  278 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4680),  $\delta_{\text{H}}(\text{CDCl}_3; \text{Me}_4\text{Si})$  1.68 (3 H, d,  $J$  17.6, Me), 3.66 (6 H, s, OMe), 6.93 (4 H, d,  $J$  9.28, Ar) and 7.07 (4 H, Ar);  $\delta_{\text{P}}(\text{CDCl}_3; 80\% \text{ H}_3\text{PO}_4)$  25.0 (q,  $J_{\text{HP}}$  17.1).

**4-Cyanophenyl 4-methoxyphenyl methylphosphonate 1b.** Compound **1b** was prepared by the reaction of 4-methoxyphenyl methylphosphonyl chloride and 4-cyanophenol in a manner similar to that described above, m.p. 63–65 °C (Found: C, 60.0; H, 4.7; N, 4.6; P, 10.2.  $C_{15}H_{14}NO_4P$  requires C, 59.41; H, 4.65; N, 4.62; P, 10.21%);  $\lambda_{\max}(\text{MeOH})/\text{nm}$  277 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4200);  $\delta_{\text{H}}(\text{CDCl}_3; \text{Me}_4\text{Si})$  1.80 (3 H, d,  $J$  17.6, Me), 3.79 (3 H, s, OMe) and 7.34 (8 H, m, Ar);  $\delta_{\text{P}}(\text{CDCl}_3; 80\% \text{ H}_3\text{PO}_4)$  25.0 (q,  $J_{\text{HP}}$  17.1).

**3-Cyanophenyl 4-methoxyphenyl methylphosphonate 1c.** Compound **1c**, prepared using 3-cyanophenol in a manner similar to that described above, was a colourless oil (Found: C, 59.5; H, 4.6; N, 4.6; P, 10.3.  $C_{15}H_{14}NO_4P$  requires C, 59.41; H, 4.65; N, 4.62; P, 10.21%);  $\lambda_{\max}(\text{MeOH})/\text{nm}$  277 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  4200);  $\delta_{\text{H}}(\text{CDCl}_3; \text{Me}_4\text{Si})$  1.83 (3 H, d,  $J$  17.6, Me), 3.79 (3 H, s, OMe) and 7.15 (8 H, m, Ar);  $\delta_{\text{P}}(\text{CDCl}_3; 80\% \text{ H}_3\text{PO}_4)$  25.0 (q,  $J_{\text{HP}}$  17.1).

**4-Methoxyphenyl methyl 4-chlorobenzylphosphonate 5a.** Compound **5a**, prepared using methyl 4-chlorobenzylphosphonyl chloride and 4-methoxyphenol in a manner similar to that described above, was a colourless viscous oil (Found: C, 58.4; H, 4.5; Cl, 11.7; P, 10.2.  $C_{15}H_{13}ClO_5P$  requires C, 58.55; H, 4.26; Cl, 11.52; P, 10.07%);  $\lambda_{\max}(\text{MeOH})/\text{nm}$  276 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  2000).

**Bis(4-methoxyphenyl) 4-chlorobenzylphosphonate 5b.** 4-Methoxyphenol (2 mol equiv.) was added to 4-chlorobenzylphosphonyl dichloride in the presence of triethylamine in ether, and the mixture was stirred for 2 h under reflux. After filtration, the filtrate was purified by column chromatography on silica gel to provide a colourless viscous oil (Found: C, 65.1; H, 5.3; Cl, 9.0; P, 8.0.  $C_{21}H_{20}ClPO_3$  requires C, 65.21; H, 5.21; Cl, 9.17; P, 8.01%);  $\lambda_{\max}(\text{MeOH})/\text{nm}$  277 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  2300).

### Photolysis

**General Photolysis Procedure for Isolation of Products.**—A methanolic solution of **1** or **5** ( $10^{-2} \text{ mol dm}^{-3}$ , 200  $\text{cm}^3$ ) charged in a doughnut-type cell (10 mm thick quartz) was purged of dissolved air by bubbling argon through it. After irradiation with a high-pressure Hg lamp (300 W) at ambient temperature for 1 h, the reaction mixtures were analysed by GLC or GC-MS by comparison with authentic samples prepared by other methods. The product yields were determined by GLC and using triphenylmethane as an internal standard. In some cases, the reaction products were isolated by column chromatography on silica gel and identified by elemental analysis and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

### 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 **2a** and dimethyl methylphosphonate **3b** were confirmed by comparison with the GC-retention times and the mass spectra of authentic samples, prepared by the methods described below. 2,5,4'-Trimethoxybiphenyl was isolated by the preparative TLC (silica gel, eluent; benzene);  $\delta_{\text{H}}(\text{CDCl}_3; \text{Me}_4\text{Si})$  3.84 (3 H, s, OMe), 3.80 (3 H, s, OMe), 3.75 (3 H, s, OMe), 6.81 (1 H, d,  $J$  11.0, Ar), 6.89 (1 H, s), 6.90 (1 H, d,  $J$  11.0, Ar), 6.96 (2 H, d,  $J$  9.3, Ar) and 7.47 (2 H, d,  $J$  9.3, Ar);  $\delta_{\text{C}}(\text{CDCl}_3; \text{Me}_4\text{Si})$  55.2, 55.6, 56.3,

112.5, 112.6, 113.5, 116.5, 130.4, 130.7, 131.3, 150.7, 153.7 and 158.7. These data agreed with those of an authentic sample prepared by the method described below.

**Photolysis Products of 4-Cyanophenyl 4-Methoxyphenyl Methylphosphonate 1b.**—By GC-MS analysis after methylation of the photolysis product, 4-methoxy-4'-cyanobiphenyl **2c** and **3b** were confirmed by comparison with authentic samples. A further major product **4b** [ $m/z$  317 ( $M^+$ , 100), 221 (11), 206 (11), 93 (78) and 63 (17)] was also found. After hydrolysis with an aqueous ethanolic solution (60%) of sodium hydroxide (5%), the reaction mixture was extracted with ether to give oily material, which was methylated with diazomethane and purified with column chromatography on silica gel to give a colourless oil (Found:  $M^+$ , 239.095.  $C_{15}H_{13}NO_2$  requires  $M^+$ , 239.0947);  $m/z$  239 ( $M^+$ , 100%), 224 (40), 206 (6), 193 (9), 181 (6), 153 (15), 63 (5);  $\delta_{\text{C}}(\text{CDCl}_3; \text{Me}_4\text{Si})$  55.3, 55.9, 104.2, 111.5, 113.8, 119.3, 120.6, 128.6, 130.2, 131.6, 132.7, 134.2, 159.4 and 159.8. These data agreed closely with the calculated values for 5-cyano-2,4'-dimethoxybiphenyl **2e**;  $\delta_{\text{H}}(\text{CDCl}_3; \text{Me}_4\text{Si})$  3.85 (3 H, s, OMe), 3.87 (3 H, s, OMe), 6.96 (2 H, d,  $J$  8.8, Ar), 7.00 (1 H, d,  $J$  8.3, Ar), 7.56 (1 H, s, Ar), 7.42 (2 H, d,  $J$  8.8, Ar) and 7.57 (1 H, d,  $J$  8.3, Ar).

**Photolysis Products of 3-Chlorophenyl 4-Methoxyphenyl Methylphosphonate 1c.**—After methylation, the photolysis products were analysed by GC-MS and identified as **2f** and **3b** by comparison with the spectral data of authentic samples.

**Photolysis Products of 4-Chlorophenyl 4-Methoxyphenyl Methylphosphonate 1d.**—The products were analysed with GC-MS after methylation and identified as 4-chloro-4'-methoxybiphenyl **2g** and **3b** with authentic samples. A further component was isolated by column chromatography on silica gel (eluent;  $\text{CHCl}_3$ ) and identified as methyl 4-chloro-2-(4'-methoxyphenyl)phenyl methylphosphonate **4c** as follows; colourless oil,  $m/z$  326 ( $M^+$ ) (Found: C, 55.5; H, 4.9; Cl, 10.3; P, 9.5.  $C_{15}H_{16}ClO_4P$  requires C, 55.14; H, 4.94; Cl, 10.85; P, 9.48%). It was hydrolysed and methylated in a manner similar to that described above;  $\delta_{\text{C}}(\text{CDCl}_3; \text{Me}_4\text{Si})$  55.3, 55.8, 114.6, 115.6, 127.6, 128.1, 128.4, 128.6, 128.7, 133.7, 156.8 and 158.9. These  $^{13}\text{C}$  NMR data observed agreed closely with the calculated value of 5-chloro-2,4'-dimethoxybiphenyl **4d**.<sup>12</sup>

**Photolysis Products of Methyl 4-Methoxyphenyl 4-Chlorobenzylphosphonate 5a.**—After irradiation, the reaction mixture was treated with diazomethane, and two products were isolated as colourless oils by column chromatography on silica gel in a manner similar to that described above. The first component had:  $m/z$  340 ( $M^+$ , 90%), 230 (90), 186 (100), 181 (20) and 152 (40) (Found: C, 59.25; H, 5.6; Cl, 10.9; P, 9.5.  $C_{16}H_{18}ClO_4P$  requires C, 56.40; H, 5.33; Cl, 9.09; P, 10.41%);  $\delta_{\text{C}}(\text{CDCl}_3; \text{Me}_4\text{Si})$  28.7 ( $J_{\text{CP}}$  138.7), 52.6 ( $J_{\text{CP}}$  6.9), 55.1, 113.7, 128.6 ( $J_{\text{CP}}$  3.0), 127.1 ( $J_{\text{CP}}$  3.3), 127.4 ( $J_{\text{CP}}$  8.8), 130.2, 131.0 ( $J_{\text{CP}}$  6.9), 131.6 ( $J_{\text{CP}}$  4.8), 131.9, 143.8 ( $J_{\text{CP}}$  8.2) and 159.0 and was identified as dimethyl 4-chlorobenzyl-2-(4'-methoxyphenyl)phosphonate **6a**. A second component had:  $m/z$  306 ( $M^+$ , 70%), 186 (100), 181 (20) and 165 (10) (Found: C, 62.7; H, 6.2; P, 10.05.  $C_{16}H_{19}O_4P$  requires C, 62.74; H, 6.25; P, 10.11%) and was identified as methyl 2-(4'-methoxyphenyl)benzylphosphonate **6b**.

**Photolysis of the Products of Bis(4-methoxyphenyl) 4-Chlorobenzylphosphonate 5b.**—After irradiation, the reaction mixture was treated with diazomethane and the product mixture was analysed with GC-MS by comparison with the retention times and mass patterns with those of authentic samples; **2a**, 2,5,4'-trimethoxybiphenyl **2b**, and dimethyl 4-chlorobenzylphosphonate **3d**. Two other components were isolated by column chromatography on silica gel (eluent;  $\text{CHCl}_3$ ) as viscous oils. The first component **6c** had:  $m/z$  432

(M<sup>+</sup>, 70%), 309 (100), 230 (20), 196 (80) and 181 (20) (Found: C, 61.2; H, 5.3; Cl, 7.4; P, 8.1. C<sub>22</sub>H<sub>22</sub>ClO<sub>5</sub>P requires C, 61.05; H, 5.12; Cl, 7.16; P, 8.19%). It was hydrolysed with aqueous sodium hydroxide (5%) for 24 h and, after acidification, the product was extracted with ether. The residue, after methylation with diazomethane, was analysed with GC-MS and identified as **6a** in a manner similar to that described above. Therefore, **6c** was identified as methyl 4-methoxyphenyl 2-(4'-methoxyphenyl)-4-chlorobenzylphosphonate. A further component **6d** had: *m/z* 298 (M<sup>+</sup>, 70%), 275 (100), 243 (10) and 196 (40) (Found: C, 66.2; H, 5.8; P, 7.7. C<sub>22</sub>H<sub>23</sub>O<sub>5</sub>P requires: C, 66.33; H, 5.82; P, 7.78%). It was treated in a similar manner to **6c** and gave methyl 4-methoxyphenyl 2-(4'-methoxyphenyl)benzylphosphonate **6b** as the compound isolated.

*Preparation of Authentic Samples.*—Dimethyl 4-chlorobenzylphosphonate **3d**. The phosphonate **3d** was prepared from 4-chlorobenzylphosphonyl dichloride by the procedure reported.<sup>13</sup>

4,4'-Dimethoxybiphenyl **2a**. Compound **2a** was prepared by methylation of 4,4'-dihydroxybiphenyl with dimethyl sulfate in alkaline aqueous solution; it had m.p. 201–202 °C (Found: C, 78.55; H, 6.6. C<sub>14</sub>H<sub>14</sub>O<sub>2</sub> requires C, 78.48; H, 6.59%).

2,5,4'-Trimethoxybiphenyl **2b**. Compound **2b** was prepared by *p*-methoxyphenylation of 1,4-dimethoxybenzene. The reaction was carried out with 4-methoxybenzenediazonium tetrafluoroborate and 1,4-dimethoxybenzene at a molar ratio of 1:30 at 230 °C for 4 h.<sup>14</sup> The GC-MS spectrum and <sup>1</sup>H and <sup>31</sup>P NMR data agreed with those of **2b** isolated from the photolysis of **1a** or **5b**.

4-Cyano-4'-methoxybiphenyl **2c**.—Compound **2c** was prepared by cyanation of 4-bromo-4'-methoxybiphenyl with cuprous cyanide<sup>15</sup> (Found: C, 80.3; H, 5.25; N, 6.7. C<sub>14</sub>H<sub>11</sub>NO requires C, 80.36; H, 5.30; N, 6.69%); δ<sub>C</sub>(CDCl<sub>3</sub>; Me<sub>4</sub>Si) 111.9, 114.5, 128.0, 128.4, 132.5, 133.9, 145.5 and 158.7.

3-Cyano-4'-methoxybiphenyl **2f**. *p*-Anisidine was diazotized with sodium nitrite in hydrochloric acid solution at 0 °C.<sup>16</sup> To the stirred and cooled solution of the diazonium salt and benzonitrile 5 mol dm<sup>-3</sup> aqueous sodium hydroxide solution was added during the course of 1 h. After 8 h of continued stirred a heavy brown oil was obtained and this was flash chromatographed on silica gel and then distilled *in vacuo* (130–140 °C/2 mmHg). The pure product was obtained by recrystallization from methanol, m.p. 82–83 °C (Found: C, 80.6; H, 5.3; N, 6.7. C<sub>14</sub>H<sub>11</sub>NO requires C, 80.36; H, 5.30; N, 6.69%); δ<sub>C</sub> 113.5, 114.5, 128.4, 129.5, 130.6, 130.9, 131.0, 133.9, 142.2 and 158.7.

4-Chloro-4'-methoxybiphenyl **2g**. Compound **2g** was prepared by chlorophenylation of anisole with 4-chlorobenzene-diazonium chloride as reported previously;<sup>17</sup> it had m.p. 110–111 °C.

*Measurement of Quantum Yield.*—The quantum yields were measured as follows. A 3 cm<sup>3</sup> methanol solution of the substrate (1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>) 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 within 10% conversion. Actinometry was carried on a potassium trioxalatoferate(III) solution<sup>18</sup> and the product yield was determined by GLC.

*Quenching of Fluorescence with Oxygen.*—Six 3-cm<sup>3</sup> aliquots of the substrate in methanol (1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>) were charged in six separate quartz cells (10 mm × 10 mm). Argon, air, 40, 60, 80% oxygen/nitrogen or pure oxygen gas, respectively, were bubbled into the solutions at 20 °C for 10 min, to ensure saturation. Concentrations of oxygen in these solutions were evaluated from their solubilities in methanol as 0.0, 1.51, 3.82, 5.72, 7.63 and 9.54 × 10<sup>-3</sup> mol dm<sup>-3</sup>, respectively.

Their emission spectra were recorded on a fluorescence spectrometer.

*Quenching of Quantum Yield of Product with Oxygen.*—Six 3-cm<sup>3</sup> aliquots of the substrate (1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>) in methanol saturated with the prescribed concentration of oxygen were prepared, respectively, and their quantum yields were measured in a manner similar to that described above.

*Solvent Effect.*—Quantum yields of the product were measured for solutions in methanol, ethanol, acetonitrile, 1,4-dioxane and ether. Thus, 2-cm<sup>3</sup> aliquots of the substrate (2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>) dissolved in these solvents were introduced into quartz tubes (diam. 10 mm). After argon had been bubbled through each solution to purge dissolved air, it was irradiated in a merry-go-round apparatus with a high-pressure Hg lamp at ambient temperature for 1 h. The reaction products were then analysed by GLC directly or after treatment with diazomethane-ether solution. The yields were determined using triphenylmethane as an internal reference. Some authentic samples for GLC were commercially available and the others were prepared by the methods described above.

*Addition Effect of Acetic Acid.*—UV irradiation and analysis were made on two 3-cm<sup>3</sup> acetonitrile solutions of the substrate (1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>) containing acetic acid at concentrations of 0.0, 50 and 100 × 10<sup>-3</sup> mol dm<sup>-3</sup> in a manner similar to that described.

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