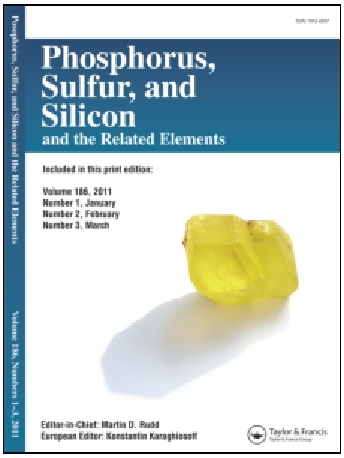

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHOTOLYSIS OF ARYL ESTERS OF TRI- AND TETRACOORDINATE PHOSPHORUS COMPOUNDS

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To cite this Article Shi, Min , Yamamoto, Kiichi , Okamoto, Yoshiki and Takamuku, Setsuo(1991) 'PHOTOLYSIS OF ARYL ESTERS OF TRI- AND TETRACOORDINATE PHOSPHORUS COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 60: 1, 1 — 14

To link to this Article: DOI: 10.1080/10426509108233919

URL: http://dx.doi.org/10.1080/10426509108233919

Phosphorus, Sulfur, and Silicon, 1991, Vol. 60, pp. 1–14
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PHOTOLYSIS OF ARYL ESTERS OF TRI- AND TETRACOORDINATE PHOSPHORUS COMPOUNDS

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(Received September 10, 1990; in final form October 20, 1990)

Upon UV excitation in methanol, some diaryl esters of alkyl- or alkenylphosphonates underwent an elimination of two aryl groups to give biaryls and the corresponding alkyl- or alkenylphosphonic acids. Tris(4-methoxyphenyl) phosphite also underwent a similar elimination to give 4,4′-dimethoxybiphenyl and 4-methoxyphenyl phosphonate. This interesting biaryl elimination was confirmed to proceed via a singlet intramolecular excimer by means of fluorescence spectra and Stern-Volmer analysis.

Key words: Photolysis; bis(4-methoxyphenyl) alkylphosphonate; bis(4-methoxyphenyl) styrylphosphonate; tris(4-methoxyphenyl) phosphite; fluorescence spectrum; 4,4′-dimethoxybiphenyl

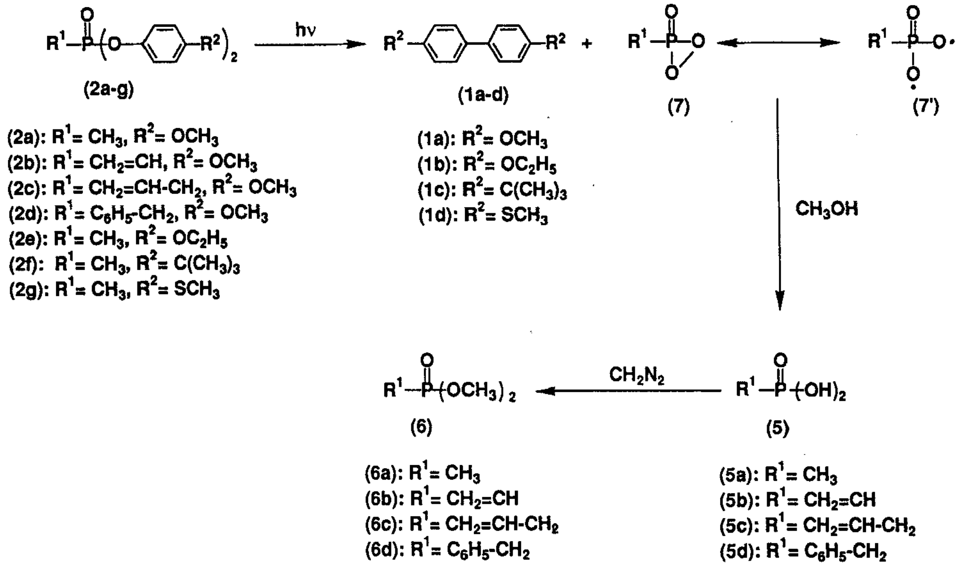
INTRODUCTION

It has already been reported that upon UV irradiation, some triaryl phosphates underwent an intramolecular elimination of two aryl groups to afford biaryls (**1**) and aryl phosphates. This photochemical reaction was concluded to proceed via a concerted fashion, or coupling between the fragments which were contained very tightly within a solvent cage.[1] We have also reported the formation of biaryls by photolysis of dimethyl triarylmethylphosphonates.[2,3] This interesting photochemical behavior of the organophosphorus compounds stimulated further study of the photolysis of other tetracoordinate phosphorus compounds, diaryl esters of alkyl- or alkenylphosphonate (**2**) and a tricoordinate phosphorus compound, tris(4-methoxyphenyl) phosphite (**3**). Their polymerized products are of interest in photoresist applications.

We now wish to report the scope and limitation of the photolysis of **2** and **3**. Furthermore, photolysis of a tetraaryl pyrophosphate (**4**) was also examined. In addition, the mechanism of the biaryl elimination reaction is discussed on the basis of the spectral data.

RESULTS AND DISCUSSION

The photolyses of methanol solutions of **2a-g** (1.0×10^{-2} mol dm^{-3}) were carried out in quartz tubes by use of a high pressure mercury lamp (300 W) with a Vycor filter at ambient temperature under argon atmosphere. We found that upon UV excitation, two 4-methoxyphenyl, 4-ethoxyphenyl, 4-t-butylphenyl or 4-methylthiophenyl groups of **2a-g** were effectively eliminated in each case, to give 4,4′-dimethoxybiphenyl (**1a**), 4,4′-diethoxybiphenyl (**1b**), 4,4′-di-t-butylbiphenyl (**1c**) or 4,4′-dimethylthiobiphenyl (**1d**), respectively, and corresponding alkyl- or alkenylphosphonic acids (**5**), which were identified after being converted to the corresponding dimethyl alkyl- or alkenylphosphonates (**6**) by treatment with an ethereal solution of diazomethane (Scheme 1).



Scheme 1.

The products (**5**) might be derived from the "peroxidized" phosphorus species **7** or the dioxy radical species **7′**, which reacts with the methanol in a manner similar to that described in the literature.[1] The product yields on photolyses of **2a-g** after 1 h irradiation are summarized in Table I.

Figure 1 shows the yields of **1a** and dimethyl benzylphosphonate (**6d**), which were measured after treatment of the reaction mixture with diazomethane, and

TABLE I

Photolysis of (2a–g) in methanol[a]

Compd. (2a-g)	R^1	R^2	Conv./%	Φ[b]	Product/% (1)	(5)[c]
(2a)	CH_3	OCH_3	73	0.12	70	64
(2b)	CH_2=CH	OCH_3	86	0.10	84	80
(2c)	CH_2=CH-CH_2	OCH_3	55	0.064	50	50
(2d)	C_6H_5-CH_2	OCH_3	70	0.10	66	58
(2e)	CH_3	OC_2H_5	65	0.093	58	54
(2f)	CH_3	$C(CH_3)_3$	40	0.050	36	30
(2g)	CH_3	SCH_3	80	0.16	80	78

a) Irradiated in a quartz tube for 1 h.
b) The quantum yields of (1).
c) The yields of 5 were based on the formation of (6).

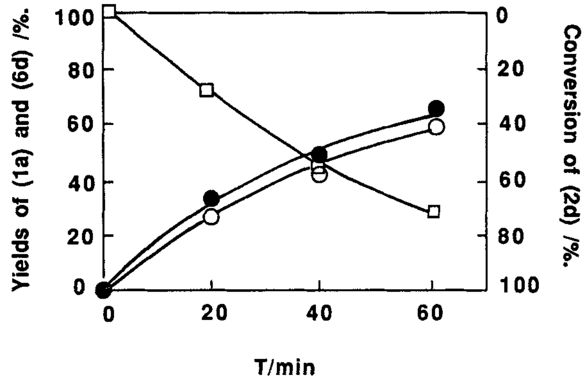


FIGURE 1 Photolysis of bis(4-methoxyphenyl) benzylphosphonate (**2d**) in methanol. ●: (**1a**); ○: (**6d**); □: (**2d**).

the conversion of bis(4-methoxyphenyl) benzylphosphonate (**2d**) as a function of irradiation time. The yields of **1a** and **6d** increased almost linearly with the lapse of irradiation time with a conversion of less than 30%. This fact indicates that they were primary products.

The solvent effect upon photolysis of **2d** was also examined, and it was revealed that the chemical and quantum yield of **1a** in polar solvents were larger than those of **1a** in a nonpolar solvent (Table II).

In contrast to **2a-g**, it is worth noting that when trans-styrylphosphonate (**2h**) was irradiated under the same conditions, no **1a** could be detected by GLC. A mixture of **2h** and bis(4-methoxyphenyl) cis-styrylphosphonate (**2h'**) was observed. The latter was apparently derived from **2h** by a photo-induced isomerization (Scheme 2). This photoreaction is due to the localization of excitation energy to the styryl chromophore, the energy level of which is lower than that of the methoxyphenyl chromophore. Bis(4-methoxyphenyl) phenylphosphonate (**2i**) was also quite stable for irradiation, because it may also have a chromophore, the phenylphosphinyl moiety, having a lower excitation energy level.

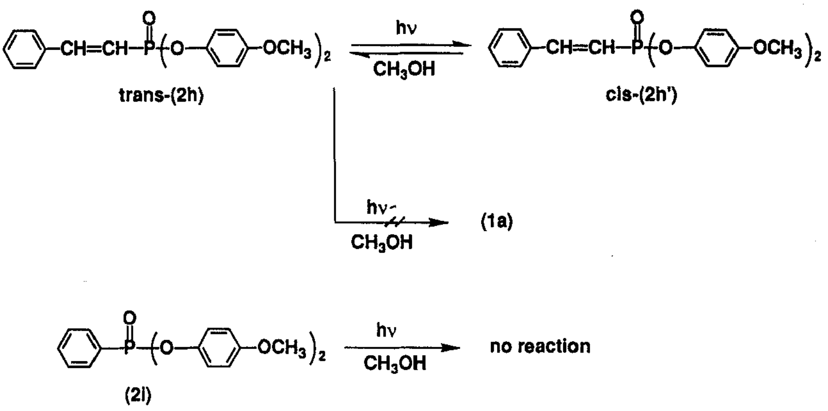
Upon UV irradiation of ethyl bis(4-methoxyphenyl) phosphate (**2j**) or ethyl bis(4-

TABLE II

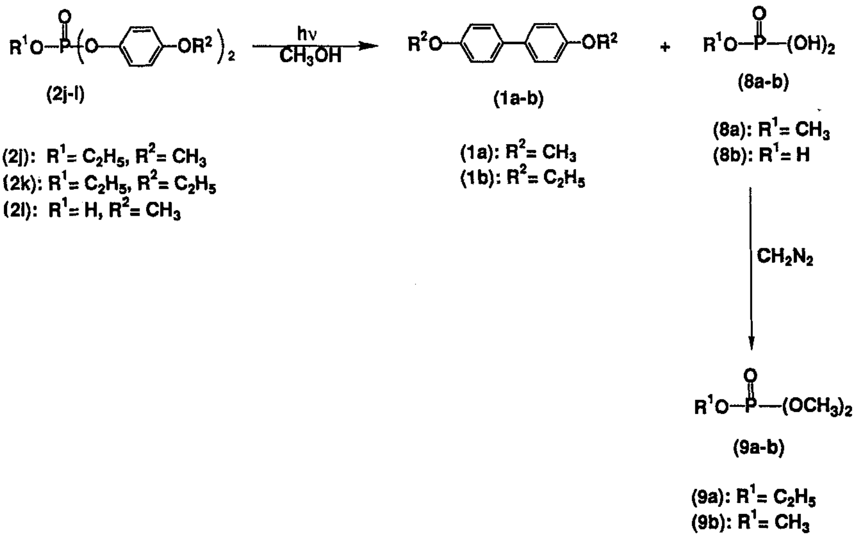
Photolysis of (2d) in various solvents[a]

Solvent	$\Phi^{b)}$	Conv./%	Product/%	
			(1a)	(6d)
Methanol	0.1	70	66	58
Acetonitrile	0.12	75	68	60
Tetrahydrofuran (THF)	0.06	50	48	44
Cyclohexane	0.02	30	15	11

a) Irradiated in a quartz tube for 1h.
b) The quantum yield of (1a).



Scheme 2.



Scheme 3.

TABLE III

Photolysis of (2j–1) in methanol[a]

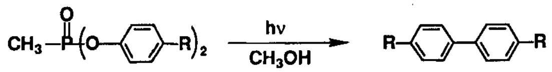
Compd.	Conv./%	$\Phi^{b)}$	Product/% (1a) or (1b)
(2j)	75	0.13	70
(2k)	78	0.14	71
(2l)	80	0.14	75

a) Irradiated in a quartz tube for 1 h.
b) The quantum yields of (1).

ethoxyphenyl) phosphate (**2k**) in methanol, the same photochemical reaction took place to give **1a** or **1b** and ethyl phosphate (**8a**), respectively. Bis(4-methoxyphenyl) phosphate (**2l**) gave **1a** and orthophosphoric acid (**8b**) in almost the same quantum yields as described in Scheme 1. Structures (**8a**) and (**8b**) were confirmed after converting into the corresponding methyl esters **9a** and **9b** in the same manner as described above (Scheme 3, Table III).

When diphenyl methylphosphonate (**2m**), di-p-tolyl methylphosphonate (**2n**), and bis(4-chlorophenyl) methylphosphonate (**2o**) were irradiated under the same conditions, only trace amounts (4–6%) of **1** could be detected (Scheme 4). These results clearly suggest that the introduction of electron donating substituents in the phenyl groups favors the elimination of **1** from **2**.

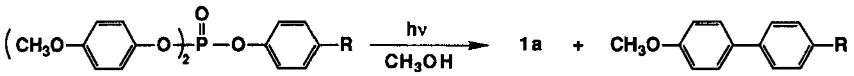
Some unsymmetrical triaryl phosphates such as bis(4-methoxyphenyl) p-tolyl phosphate (**2p**) and p-chlorophenyl bis(4-methoxyphenyl) phosphate (**2q**) were also prepared and their photolyses were carried out in the same manner as described above (Scheme 5). As the results, it was found that **2p** gave two product types, a symmetrical biaryl, **1a**, and an unsymmetrical biaryl, 4-methoxy-4′-methylbiphenyl (**1e**), respectively. However, **2q** afforded only an unsymmetrical biaryl, 4-chloro-4′-methoxybiphenyl (**1f**). Their yields are shown in Table IV. The interaction between 4-methoxyphenyl and 4-chlorophenyl groups may be much stronger than that between two 4-methoxyphenyl groups in **2q**.



(2m-o) 4-5%

(2m): R= H
(2n): R= CH_3
(2o): R= Cl

Scheme 4.



(2p-q) (1e-f)

(2p): R= CH_3
(2q): R= Cl

(1e): R= CH_3
(1f): R= Cl

Scheme 5.

TABLE IV

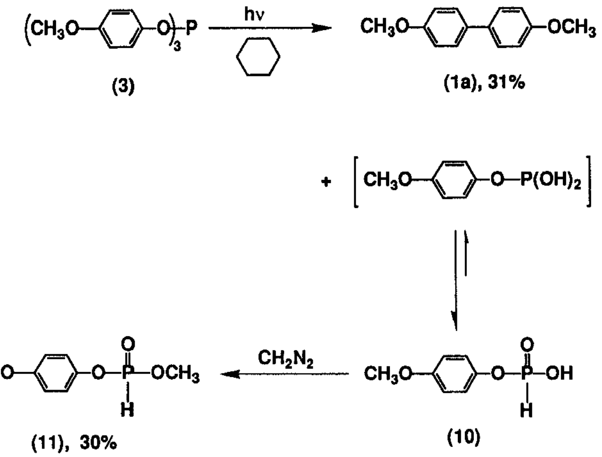
Photolysis of (2p–q) in methanol[a]

Compd.	Φ[b]	Conv./%	Product/% (1a)	Product/% (1e) or (1f)
(2p)	0.13	80	46	25
(2q)	0.10	82	trace	50

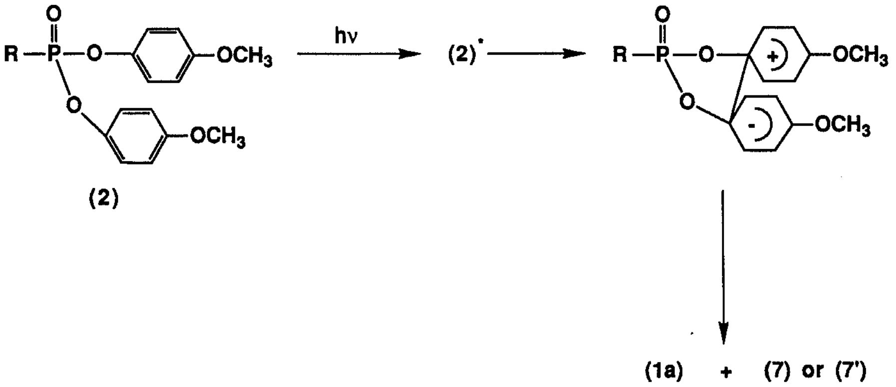
a) Irradiated in a quartz tube for 1 h.
b) The quantum yield of (1).

Furthermore, UV irradiation of the tricoordinate phosphorus compound, tris(4-methoxyphenyl) phosphite (**3**), in cyclohexane or acetonitrile (very labile in protic solvents) also afforded **1a** and 4-methoxyphenyl phosphonate (**10**), which was similarly confirmed as 4-methoxyphenyl methyl phosphonate (**11**) after treatment with an ethereal solution of diazomethane (Scheme 6). This result suggests that biaryl elimination from **2** occurs only by means of the interaction of two aryl groups and independent of the participation of the phoshoryl bond (P═O) in the transient intermediate as proposed by Finnegan and his coworkers.[1]

The elimination of two aryl groups from **2** or **3** can be explained through an intramolecular interaction between two aryl groups (Scheme 7).[1] In order to obtain the information concerning this interaction, namely the existence of intramolecular excimer, the fluorescence studies of **2j** were performed. In Figure 2, a fluorescence spectrum of **2j** in methanol (2.0 × 10^{-3} mol dm^{-3}) at ambient temperature is shown. This spectrum did not be changed, even if the solution was diluted with methanol tenfold.



Scheme 6.



Scheme 7.

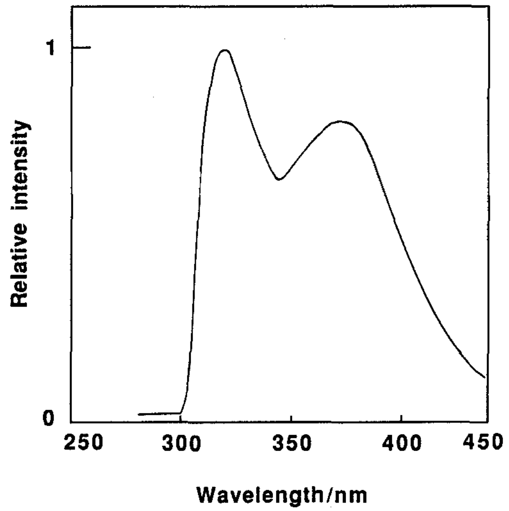
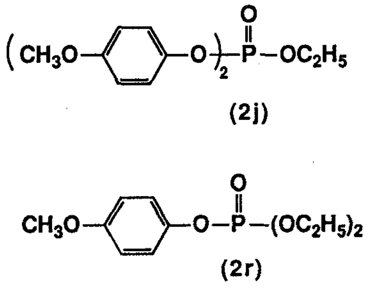


FIGURE 2 The fluorescence spectrum of bis(4-methoxyphenyl) ethyl phosphate (**2j**) in methanol (2.0 × 10^{-3} mol dm^{-3}), (λ ex = 250 nm).



(2j)

(2r)

Formula of (2j) and (2r).

The fluorescence spectrum of diethyl 4-methoxyphenyl phosphate (**2r**) was also measured under the same conditions as described above (Figure 3). By comparison of both spectra it is clear that the emissions at 370 and 314 nm are attributable to an intramolecular excimer and a monomer of 4-methoxyphenyl group, respectively. Moreover, the addition of molecular oxygen into the methanol solution of **2j** quenched the fluorescence of **2j**. As the result of Stern-Volmer analysis of this quenching experiment, $k_q \tau$ = 222 dm^3 mol^{-1} (correlation coefficient: R = 0.9840) and $k_q \tau$ = 140 dm^3 mol^{-1} (R = 0.9998) were obtained for the excimer (370 nm) and the monomer (310 nm), respectively. Similarly, when the photolyses of the methanol solutions of **2j** containing various concentrations of molecular oxygen were carried out under the same conditions, we found that the yield of **1a** gradually decreased with increase of oxygen concentration. The Stern-Volmer analysis of photo-product gave $k_q \tau$ = 262 dm^3 mol^{-1} (R = 0.9855), which was very similar to that obtained

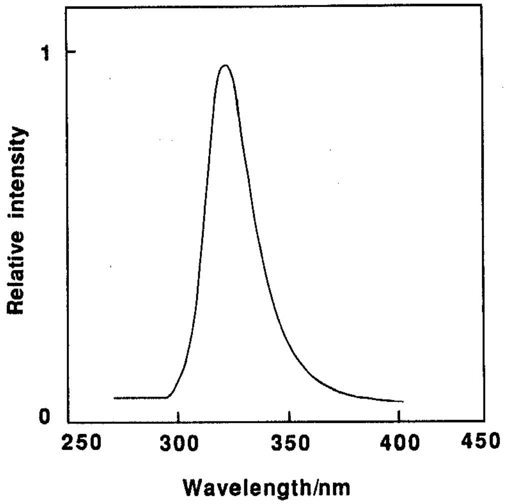


FIGURE 3 The fluorescence spectrum of 4-methoxyphenyl diethyl phosphate (**2r**) in methanol (2.0 × 10^{-3} mol dm^{-3}), (λ ex = 250 nm).

in the excimer fluorescence quenching experiment. Furthermore, in order to identify the presence of a monomer*-excimer* equilibrium, the lifetimes of fluorescences of monomer* and excimer* were measured by use of a single photon counting system (Figures 4 and 5). The lifetimes of the excimer* (370 nm) and the monomer* (310 nm) were 9.8 and 5.0 ns, respectively. This result suggests that the presence of a quick equilibrium between the monomer* and the excimer* is denied. Therefore, it is clear that the photo-induced biaryl elimination from **2** or **3** undoubtedly proceeds via a singlet intramolecular excimer excited state.

This intramolecular process is also supported by Finnegan's crossover experiment

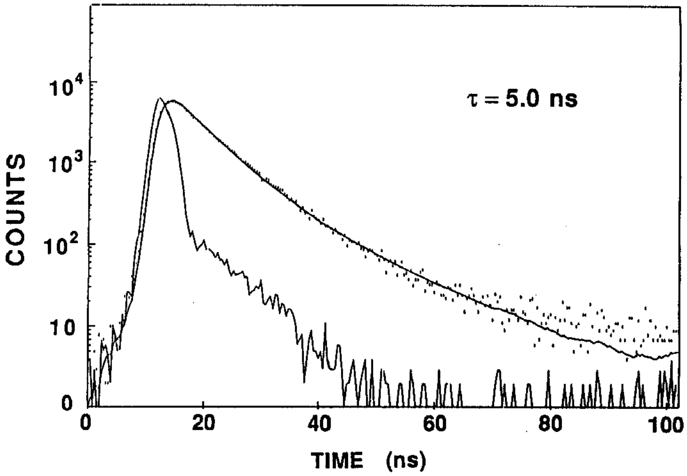


FIGURE 4 The fluorescence lifetime of the monomer of **2j** (2.0 × 10^{-3} mol dm^{-3}) (λ_{max} = 310 nm) obtained by use of a single photon counting system.

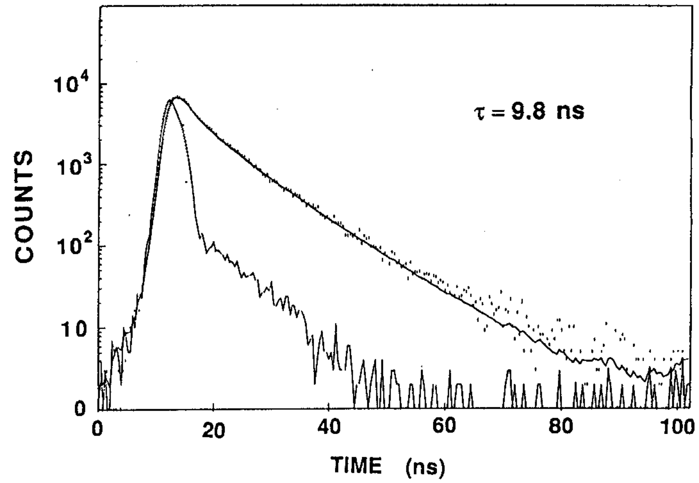


FIGURE 5 The fluorescence lifetime of the excimer of **2j** (2.0×10^{-3} mol dm^{-3}) (λ_{max} = 370 nm) obtained by use of a single photon counting system.

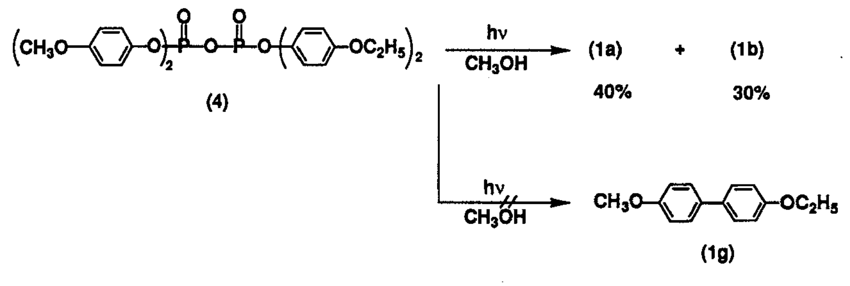
for an equimolar mixture of triphenyl and tris(4-methylphenyl) phosphate in ethanol solution, in which only biphenyl and 4,4′-dimethylbiphenyl were obtained.[1]

An intramolecular excimer of two aromatic rings has been observed in the type Ar-$(CH_2)_n$-Ar′, and often for n = 3 an optimal situation is obtained.[4]

The situation of diaryl groups in **2** or **3**, which is separated by three atoms (—O—P—O—), may satisfy the requirement for this intramolecular excimer formation.

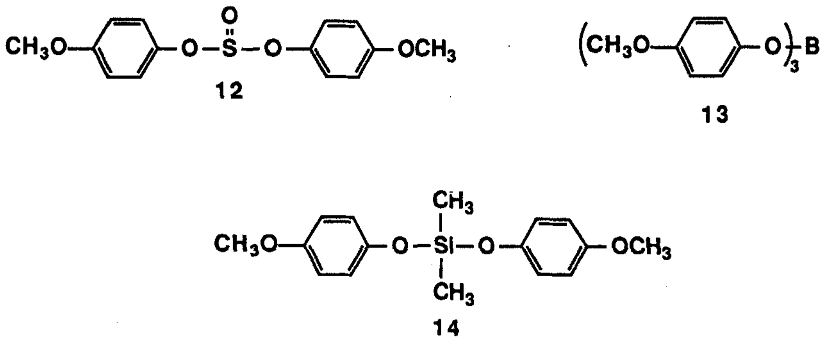
Upon UV irradiation of a methanol solution of 1,1-bis(4-ethoxyphenyl) 3,3-bis(4-methoxyphenyl) pyrophosphate (**4**), two kinds of symmetric biaryl compounds, **1a** and **1b**, were obtained, but no cross coupling biaryl, 4-methoxy-4′-ethoxybiphenyl (**1g**), was detected (Scheme 8).

This may be due to the fact that the ethoxyphenyl and methoxyphenyl groups are separated by five atoms (—O—P—O—P—O—). Therefore, the interaction between them would not be expected.



Scheme 8.

In order to investigate the scope and limitation of this interesting biaryl elimination, some other compounds having the bond structure of —O—X—O—, such as bis(4-methoxyphenyl) sulfate (X=S, **12**), tris(4-methoxyphenyl) borate (X=B, **13**), and bis(4-methoxyphenoxy)dimethylsilane (X=Si, **14**), were prepared. Even upon prolonged UV irradiation under the same conditions as described above, trace amounts of **1a** could not be detected by GLC. Furthermore, the intramolecular excimer band was not observed in the fluorescence spectrum of **12**, **13**, or **14**. These results suggest that, this type of photo-induced biaryl elimination requires a specific geometrical relationship between two aryl groups. Only phosphorus compunds may possess a satisfactory configuration for this elimination.



12

13

14

Formula of 12, 13 and 14

EXPERIMENTAL

Mps and bps were obtained with a Yanagimoto micro melting point apparatus and were uncorrected. UV-visible spectra were recorded with a Hitachi 150–20 using MeOH solvent. Steady-state fluorescence spectra were recorded with a Hitachi 850 type fluorescence spectrophotometer. Microanalyses were carried out by means of a Perkin-Elmer Model 240 analyzer. ^{1}H NMR spectra were determined as solutions in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard on a Bruker-AM360. ^{31}P NMR spectra were recorded on a JNM FX 100 with 85% H_3PO_4 as an internal standard. IR spectra were determined as KBr disks using a Hitachi Model 345. GLC analyses were carried out using a 2% Silicon OV-17 on Chrom WAW DMCS (60/80 mesh) with a Shimadzu Model 7A instrument. GC-MS spectra were recorded with a JNS-DX300 instrument. Some authentic samples were commercially available, and the others were prepared by the known methods (see below). The yields were determined using methyl diphenylacetate as an internal standard.

Preparation of bis(4-methoxyphenyl), bis(4-ethoxyphenyl), bis(4-methylthiophenyl), or bis(4-t-butylphenyl) alkyl-, alkenyl-, and phenylphosphonates (**2a-i**). The compounds (**2a-i**) were prepared by the reactions of corresponding alkyl-, alkenyl or phenylphosphonyl dichlorides (50 mmol) with 2 eq. amounts of 4-methoxyphenol (4-ethoxyphenol or 4-methylthiophenol) at 160°C for 6h, respectively. After cooling, the mixtures were washed with 20% aqueous sodium hydroxide solutions and subsequently with water. Then the crude products were purified by means of flash chromatography (eluant: hexane/chloroform = 2:1).

Bis(4-methoxyphenyl) methylphosphonate (**2a**). (12.6 g, 82%); λ_{max}(MeOH) = 278 nm (ε 4680 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1219 cm^{-1} (P=O); ^{1}H NMR (360 MHz, $CDCl_3$, TMS) δ = 1.68 (3H, d, J_{PH} = 18 Hz, Me), 3.66 (6H, s, OMe), 6.44–7.42 (8H, m, Ar); Found: m/z 308.0810 (M$^+$). $C_{15}H_{17}PO_5$: requires 308.0813.

Bis(4-methoxyphenyl) vinylphosphonate (**2b**). (12.8 g, 80%); λ_{max}(MeOH) = 278 nm (ε 4000 dm^3 mol^{-1} cm^{-1}); IR (Neat 1220 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 3.76 (6H, s, OMe), 5.43–6.60 (3H, m, CH$_2$=CH—), 6.80–7.90 (8H, m, Ar); Found: m/z 320.0810 (M$^+$). $C_{16}H_{17}PO_5$: requires 320.0813.

Bis(4-methoxyphenyl) allylphosphonate (**2c**). (12.1 g, 76%); λ_{max}(MeOH) = 277 nm (ε 3800 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1218 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 3.06 (2H, dd, J_{PH} = 22 Hz, J_{HH} = 8 Hz, —CH$_2$—), 3.80 (6H, s, OMe), 5.20–6.20 (3H m, CH$_2$═CH—), 6.80–7.90 (8H, m, Ar); Found: m/z 334.0962 (M$^+$). $C_{17}H_{19}PO_5$: requires 334.0969.

Bis(4-methoxyphenyl) benzylphosphonate (**2d**). (15.3 g, 80%); λ_{max}(MeOH) = 280 nm (ε 3550 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1214 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 3.35 (2H, d, J_{PH} = 20 Hz, —CH$_2$—), 3.63 (6H, s, OMe), 6.30–7.30 (13H, m, Ar); $_P$(360 MHz, MeOH, 85% H$_3$PO$_4$) 17.70 (t, J_{PH} = 20 Hz); Found: m/z 384.1120 (M$^+$). $C_{21}H_{21}PO_5$ requires 384.1126.

Bis(4-ethoxyphenyl) methylphosphonate (**2e**). (13.8 g, 80%); λ_{max}(MeOH) = 281 nm (ε 3600 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1216 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 1.35 (6H, t, J_{HH} = 7.0 Hz, Me), 1.69 (3H, d, J_{PH} = 18.0 Hz, Me), 4.02 (4H, q, J_{HH} = 7.0 Hz, CH$_2$), 7.00–7.40 (8H, m, Ar); Found: m/z 336.1122 (M$^+$). $C_{17}H_{21}PO_5$: requires 336.1126.

Bis(4-t-butylphenyl) methylphosphonate (**2f**). (15.0 g, 83%); λ_{max}(MeOH) = 272 nm (ε 1600 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1220 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 1.26 (18H, s, Me$_3$C), 1.72 (3H, d, J_{PH} = 20 Hz, Me), 7.0–7.40 (8H, m, Ar); Found: m/z 360.1848 (M$^+$). $C_{21}H_{29}PO_3$: requires 360.1853.

Bis(4-methylthiophenyl) methylphosphonate (**2g**). (11.6 g, 75%); λ_{max}(MeOH) 284 nm (ε 4000 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1222 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 1.84 (3H, d, J_{PH} = 20 Hz, Me), 3.86 (6H, s, MeS), 7.0–7.40 (8H, m, Ar); Found: m/z 311.0611 (M$^+$). $C_{15}H_{17}S_2O_3$: requires 311.0619.

Bis(4-methoxyphenyl) trans-styrylphosphonate (**2h**). (13.9 g, 70%); λ_{max}(MeOH) = 266 nm (ε 38000 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1220 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 3.74 (6H, s, Me), 6.44 (1H, t, J_{PH}═J_{HH} = 17.6 Hz, CH═), 6.80–7.38 (13H, m, Ar), 7.65 (1H, dd, J_{PH} = 23.4 Hz, J_{HH} = 17.6 Hz, CH═); Found: m/z 396.1123 (M$^+$). $C_{22}H_{21}PO_5$: requires 396.1126.

Bis(4-methoxyphenyl) phenylphosphonate (**2i**). (14.8 g, 80%); λ_{max}(MeOH) = 273 nm (ε 4000 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1218 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 3.65 (6H, s, Me), 6.42–8.10 (13H, m, Ar); Found: m/z 370.0964 (M$^+$). $C_{20}H_{19}PO_5$: requires 370.0969.

Preparation of bis(4-methoxyphenyl) or bis(4-ethoxyphenyl) phosphates (2j–1)

Ethyl bis(4-methoxyphenyl) phosphate (**2j**). The compound (**2j**) was prepared by the reactions of bis(4-methoxyphenyl) phosphoryl chloride (50 mmol) (prepared from phosphoryl chloride with 2 eq. 4-methoxyphenol, bp 230°C/0.1 mmHg) with an eq. amount of ethanol at the presence of triethylamine (10 mmol) in ether. After filtration of triethylammonium chloride, the solvent was distilled off in vacuo. Then the crude products were purified by means of a flash chromatography (eluant: hexane/chloroform = 2: 1). (15.4 g, 90%); λ_{max}(MeOH) = 273 nm (ε 3600 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1220 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 1.32 (3H, t, J_{HH} = 7.0 Hz, Me), 4.22 (2H, dq, J_{PH} = 7.2 Hz, J_{HH} = 7.0 Hz, CH$_2$), 3.65 (6H, s, OMe), 7.0–7.40 (8H, m, Ar); Found: m/z 338.0914 (M$^+$). $C_{16}H_{19}PO_6$: requires 338.0919.

Bis(4-ethoxyphenyl) ethyl phosphate (**2k**). (16.0 g, 93%); λ_{max}(MeOH) = 280 nm (ε 3500 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1216 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 1.30 (3H, t, J_{HH} = 7.0 Hz, Me), 1.35 (6H, t, J_{HH} = 7.0 Hz, Me), 4.06 (4H, q, J = 7.0 Hz), 4.20 (2H, quint, J_{HH}═J_{PH} = 7.0 Hz), 7.0–7.50 (8H, m, Ar); Found: m/z 366.1228 (M$^+$). $C_{18}H_{23}PO_6$: requires 366.1231.

Bis(4-methoxyphenyl) phosphate (**21**). The compound (**21**) was prepared by the hydrolysis of bis(4-methoxyphenyl) phosphoryl chloride (prepared from phosphoryl chloride with 2 eq. 4-methoxyphenol. bp 230°C/0.1 mmHg) in acetone.[5] (14.9 g, 96%); mp 86–90°C; λ_{max}(MeOH) = 274 nm (ε 3500 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1216 cm^{-1} (P═O); ^{1}H NMR (360 MHz, CDCl$_3$, TMS) δ = 3.38 (1H, s, OH), 3.65 (6H, s, OMe), 7.0–7.40 (8H, m, Ar); Found: m/z 310.0601 (M$^+$). $C_{14}H_{15}PO_6$: requires 310.0606.

Preparation of other diaryl alkylphosphonates **(2m–o)**. The compound **(2m–o)** were prepared in the same manner as described in the preparation of **2a**.

Diphenyl methylphosphonate **(2m)**. (10.0 g, 80%); λ_{max}(MeOH) = 261 nm (ε 760 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1216 cm^{-1} (P=O); ^{1}H NMR (360 MHz, $CDCl_3$, TMS) δ = 1.63 (3H, d, J_{PH} = 18 Hz, Me), 6.30–7.20 (10H, m, Ar); Found: m/z 248.0600 (M$^+$). $C_{13}H_{13}PO_3$: requires 248.0602.

Di-p-tolyl methylphosphonate **(2n)**. The compound **(2n)** was prepared in the same manner as described above. (9.3 g, 65%); λ_{max}(MeOH) 265 nm (ε 1300 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1210 cm^{-1} (P=O); ^{1}H NMR (360 MHz, $CDCl_3$, TMS) δ = 1.65 (3H, d, J_{PH} = 18 Hz, Me), 2.20 (6H, s, Me), 6.40–7.30 (8H, m, Ar); Found: m/z 276.0911 (M$^+$). $C_{15}H_{17}PO_3$: requires 276.0915.

Bis(4-chlorophenyl) methylphosphonate **(2o)**. The compound **(2o)** was prepared in the same manner as described above. (10.8 g, 64%); λ_{max}(MeOH) 265 nm (ε 1400 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1215 cm^{-1} (P=O); ^{1}H NMR (360 MHz, $CDCl_3$, TMS) δ = 1.68 (3H, d, J_{PH} = 18 Hz, Me), 6.40–7.60 (8H, m, Ar); Found: m/z 315.9820 (M$^+$). $C_{13}H_{11}PO_3Cl_2$: requires 315.9824.

Preparation of unsymmetric triaryl phosphate **(2p–q)**.

Bis(4-methoxyphenyl) 4-toly phosphate **(2p)**. The compound **(2p)** was prepared by the reaction of bis(4-methoxyphenyl) phosphoryl chloride (50 mmol) with 4-methylphenol (50 mmol) in the presence of triethylamine (50 mmol). After reaction, the mixture was washed with 20% aqueous sodium hydroxide solution and subsequently with water. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed off under reduced pressure. The residue was chromatographed on a silica gel column. (18.2 g, 82%); λ_{max}(MeOH) 278 nm (ε 3600 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1220 cm^{-1} (P=O); ^{1}H NMR (360 MHz, $CDCl_3$, TMS) δ = 2.21 (3H, s, Me), 3.67 (6H, s, OMe), 7.0–7.60 (12H, m, Ar); (Found: m/z 410.1074 (M$^+$). $C_{21}H_{21}PO_6$: requires 410.1075).

4-Chlorophenyl bis(4-methoxyphenyl) phosphate **(2q)**. The compound **(2q)** was prepared in the same method as described above. (18.9 g, 80%); λ_{max}(MeOH) 277 nm (ε 3650 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1220 cm^{-1} (P=O); ^{1}H NMR (360 MHz, $CDCl_3$, TMS) δ = 3.66 (6H, s, OMe), 7.0–7.60 (12H, m, Ar); Found: m/z 421.0610 (M$^+$). $C_{20}H_{19}PO_6Cl$: requires 421.0608.

Preparation of diethyl 4-methoxyphenyl phosphate **(2r)**. The compound **(2r)** was prepared by the reaction of diethyl phosphoryl chloride (50 mmol) with 4-methoxyphenol in the presence of triethylamine (50 mmol). After reaction, the mixture was treated in the same manner as described in the case of **2p**. The residue was distilled under reduced pressure. (12.0 g, 90%); bp 140°C/0.1 mmHg; ^{1}H NMR (360 MHz, $CDCl_3$, TMS) δ = 1.05 (6H, t, Me), 3.66 (3H, s, OMe), 3.82 (4H, dq, J_{HH} = 7.0 Hz, J_{HP} = 6.4 Hz, OCH_2), 7.0–7.40 (4H, m, Ar); Found: m/z 260.0813 (M$^+$). $C_{11}H_{17}PO_5$; requires 260.0813.

Preparation of tris(4-methoxyphenyl) phosphite **(3)**. The compound **(3)** was prepared by the reaction of phosphorus trichloride (50 mmol) with 3 eq. amount of 4-methoxyphenol at 120°C. After distillation under reduced pressure, **3** was obtained as colorless oil. (18.0 g, 90%); bp 260°C/0.1 mmHg; ^{1}H NMR (360 MHz, $CDCl_3$, TMS) δ = 3.65 (3H, s, OMe), 6.40–7.40 (4H, m, Ar); ^{31}P NMR (40.25 MHz, C_6H_{12}, 85% H_3PO_4) δ = 127.5(s); Found: m/z 400.1068 (M$^+$). $C_{21}H_{21}PO_6$: requires 400.1075.

Preparation of 1,1-bis(4-ethoxyphenyl) 3,3-bis(4-methoxyphenyl) pyrophosphate **(4)**. The compound **(4)** was prepared by the reaction of bis(4-methoxyphenyl) phosphoryl chloride (50 mmol) with bis(4-ethoxyphenyl) phosphate (50 mmol) [prepared by hydrolysis of bis(4-ethoxyphenyl) phosphoryl chloride (0.1 mol) in acetone. (23.4 g; 90%); mp 90–92°C, Found: C, 56.92; H, 5.78%. $C_{16}H_{19}PO_6$: requires C, 56.81; H, 5.66%] in benzene in the presence of triethylamine (50 mmol).[6] (22.4 g, 80%); λ_{max}(MeOH) 275 nm (ε 4600 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1216 cm^{-1} (P=O); ^{1}H NMR (360 MHz, $CDCl_3$, TMS) δ = 1.20 (3H, t, J_{HH} = 7.0 Hz, Me), 1.22 (3H, t, J_{HH} = 7.0 Hz, Me), 3.55 (3H, s, OMe), 3.62 (3H, s, OMe), 4.02 (2H, q, J_{HH} = 7.0 Hz), 4.08 (2H, q, J = 7.0 Hz), 7.00–7.60 (16H, m, Ar); ^{31}P NMR (40.25 MHz, THF, 85% H_3PO_4) δ = −10.9(s).

Preparation of authentic samples **(6a–d)**. The compounds **(6a–d)** were prepared by the reaction of the corresponding alkyl- or alkenyl phosphonyl chloride with methanol in the presence of triethylamine. After reaction, the mixture was washed with 20% aqueous sodium hydroxide solution and subsequently with water. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column.

Dimethyl methylphosphonate (**6a**). 80%; IR (Neat) 1214 cm^{-1} (P=O); ^1H NMR (360 MHz, $CDCl_3$, TMS) δ = 1.68 (3H, d, J_{PH} = 18 Hz, Me), 3.40 (6H, J_{PH} = 9.6 Hz, POMe); Found: m/z 124.0288 (M^+). $C_3H_9PO_3$: requires 124.0289.

Dimethyl vinylphosphonate (**6b**). 90%; IR (Neat) 1220 cm^{-1} (P=O); ^1H NMR (360 MHz, $CDCl_3$, TMS) δ = 3.40 (6H, d, J_{PH} = 9.6 Hz, OMe), 5.50–6.60 (3H, m); Found: m/z 136.0282 (M^+). $C_4H_9PO_3$: requires 136.0289.

Dimethyl allylphosphonate (**6c**). 60%, IR (Neat) 1216 cm^{-1} (P=O); ^1H NMR (360 MHz, $CDCl_3$, TMS) δ = 3.06 (2H, dd, J_{PH} = 22 Hz, J_{HH} = 8 Hz, —CH_2—), 3.38 (6H, d, J_{PH} = 10.0 Hz, OMe), 5.20–6.20 (3H, m, CH_2=CH—); Found: m/z 150.0441 (M^+). $C_5H_{11}PO_3$: requires 150.0446.

Dimethyl benzylphosphonate (**6d**). 70%; IR (Neat) 1218 cm^{-1} (P=O); ^1H NMR (360 MHz, $CDCl_3$, TMS) δ = 3.30 (2H, d, J_{PH} = 20 Hz, —CH_2—), 3.40 (6H, d, J_{PH} = 9.6 Hz, OMe), 7.0–7.40 (5H, m, Ar); Found: m/z 200.0601 (M^+). $C_9H_{13}PO_3$: requires 200.0602.

Preparation of other authentic samples (**9a**) *and* (**11**).

Ethyl dimethyl phosphate (**9a**). The compound (**9a**) was prepared by the reaction of ethyl phosphoryl dichloride with methanol in the presence of triethylamine in the same manner as described above. 60%; IR (Neat) 1220 cm^{-1} (P=O); ^1H NMR (360 MHz, $CDCl_3$, TMS) δ = 1.00 (3H, t, J = 7.0 Hz, Me), 3.40 (6H, d, J_{PH} = 10.0 Hz, OMe), 3.85 (2H, dq, J_{PH} = 7.2 Hz, J_{HH} = 7.0 Hz, CH_2); Found: m/z 154.0392 (M^+). $C_4H_{11}PO_4$: requires 154.0395.

4-Methoxyphenyl methyl phosphite (**11**). The compound (**11**) was prepared by the reaction of 4-methoxyphenyl phosphorodichloridite (prepared from phosphorus trichloride with equimolecular amount of 4-methoxyphenol at 110°C. bp 86–90°C/0.1 mmHg) with methanol. 86%; IR (Neat) 1214 cm^{-1} (P=O); ^1H NMR (360 MHz, $CDCl_3$, TMS) δ = 3.80 (3H, s, OCH_3), 3.87 (3H, d, J_{PH} = 12.0 Hz, POMe), 6.80 (1H, d, J_{PH} = 782.0 Hz, PH), 6.90 (4H, s, Ar); ^{31}P NMR (40.25 MHz, THF, 85% H_3PO_4) δ = 5.12 (dq, J_{PH} = 780.0, 8.0 Hz); Found: m/z 202.0390 (M^+). $C_8H_{11}PO_4$: requires 202.0395.

Other authentic samples were commercially available.

Bis(4-methoxyphenyl) sulfate (**12**). The compound (**12**) was prepared by the reaction of thionyl chloride with 2 eq. amounts of 4-methoxyphenol in the presence of triethylamine. After the usual workup, the crude product was purified by means of flash chromatography (elulant: hexane/chloroform = 1:1). 50%, λ_{max}(MeOH) 275 nm (ε 4600 dm^3 mol^{-1} cm^{-1}); IR (Neat) 1200 cm^{-1} (S=O); ^1H NMR (360 MHz, $CDCl_3$, TMS) δ = 3.62 (3H, s, OCH_3), 6.90–7.50 (4H, m, Ar); Found: m/z 294.2320 (M^+). $C_{14}H_{14}SO_5$: requires 294.2326.

Tris(4-methoxyphenyl) borate (**13**). This compound was prepared from boron trioxide and 3 eq. amounts of 4-methoxyphenol in benzene. The mixture was refluxed for 7 h, and then fractionally distilled, yielding 40% of **13**.[7] 64%; λ_{max}(MeOH) 276 nm (ε 4500 dm^3 mol^{-1} cm^{-1}); ^1H NMR (360 MHz, $CDCl_3$, TMS) δ = 3.62 (3H, s, OCH_3), 6.90–7.50 (4H, m, Ar); Found: m/z 380.2024 (M^+). $C_{21}H_{21}BO_6$: requires 380.2026.

Bis(4-methoxyphenoxy)dimethylsilane (**14**). The compound (**14**) was prepared by the reaction of dimethylsilyl dichloride with 2 eq. amount of 4-methoxyphenol in the presence of triethylamine. After usual workup, the residue was distillation under reduced pressure, **14** was obtained as colorless oil. 78%; bp 136°C/0.1 mmHg; λ_{max}(MeOH) 276 nm (ε 4200 dm^3 mol^{-1} cm^{-1}); ^1H NMR (360 MHz, $CDCl_3$, TMS) δ = 0.12 (6H, s, CH_3), 3.65 (6H, s, OMe), 6.40–7.40 (8H, m, Ar); Found: m/z 304.3067 (M^+). $C_{16}H_{20}SiO_4$: requires 304.3069.

A general procedure of photolysis. A 3-ml MeOH solution of **2** (1.0×10^{-2} mol dm^{-3}) was charged in a quartz tube (ϕ = 10 mm) and purged of dissolved air by purging with argon gas. It was irradiated with a merry-go-round apparatus using a high pressure mercury lamp (300 W) with a Vycor filter at ambient temperature. After irradiation of desired periods, the mixture was sampled for analysis of GLC.

The identification of the photo-products was achieved by comparison of GLC retention times and mass spectra (GC/MS) with those of the authentic samples. The product yields were determined by means of GLC calibration with triphenylmethane as an internal standard.

Fluorescence quenching experiment. A 3-ml MeOH solution of **2j** (1.0×10^{-2} mol dm^{-3}) was charged in a quartz cell (10 mm × 10 mm). Molecular oxygen [Q] was added as a quencher. The concentrations of [Q] in these tubes were adjusted to 0, 2.10, 3.72, 5.64, 7.52, and 9.40 (10^{-3} mol dm^{-3}) by purging with argon, air, 40, 60, 80 and 100% of oxygen gases, respectively. Their emission spectra were recorded on a fluorescence spectrophotometer.

Single photon counting system. The single photon counting system is composed of an optical unit [PRA(Photochemical Research Associates), 510 lamp unit, 1211 gas handing unit, 510B high voltage power supply, 1611 monochromator drive unit, Jobin-Yvon H.10C monochromator] and an electronic unit (Horiba, NAES-1100 Time-Resolved Spectro-fluoro-photometer).

Photolysis of the methanol solution of **2j** *containing molecular oxygen.* A MeOH solution of **2j** (1.0×10^{-2} mol dm^{-3}) were divided in six 3-ml portions in quartz tubes (ϕ = 10 mm). Molecular oxygen [Q] was added as a quencher. The concentrations of [Q] in these tubes were adjusted to 0, 2.10, 3.72, 5.64, 7.52, and 9.40 (10^{-3} mol dm^{-3}) by bubbling with argon, air, 40, 60, 80, and 100% of oxygen gas, respectively. They were irradiated at the same time using a merry-go-round apparatus, and the products yields were determined in the same manner as described above.

Photolysis of **4** *in MeOH.* A 3-ml MeOH solution of **4** was irradiated in the same manner as described above. This solution was stable enough to stand for several days in the dark.

Photolysis of **2d** *in various solvents.* A 3-ml solution of **2d** in cyclohexane, THF, or acetonitrile (1.0×10^{-2} mol dm^{-3}) was irradiated in the same manner as described above. After irradiation, the reaction mixture was analyzed by GLC.

Photolysis of **2a** (in a preparative scale). A 200-ml methanol solution of **2a** (1.0×10^{-2} mol dm^{-3}) was purged of dissolved air by purging with argon. It was irradiated in a quartz doughnut-type cell (10 mm thick) with a high pressure mercury lamp (300 W) for 2 h. After the reaction solution was concentrated under reduced pressure, a diazomethane ethereal solution was added. After the ether was removed off, the residue was chromatographed on silica gel using hexane and chloroform as eluants to give **1a** and **6a**. The structures of **1a** and **6a** were confirmed by comparison with the spectral data of authentic samples.

Measurement of the quantum yield. The quantum yields were measured on the basis of generated **1**. A low-pressure mercury lamp (60 W) with a Vycor filter was used as a 254-nm radiation source. A 3-ml methanol solution of **2** (1.0×10^{-2} mol dm^{-3}) in a quartz tube (10 mm × 10 mm) was irradiated. A potassium trioxalatoferrate (III) solution was used as an actinometry.[8] The yields of the products were determined by GLC (Shimadzu GC-7A, Silicone OV-17, 2%, support; Uniport HP, 1-m glass column). The photolyses were carried out at the conversion less than 5%.

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