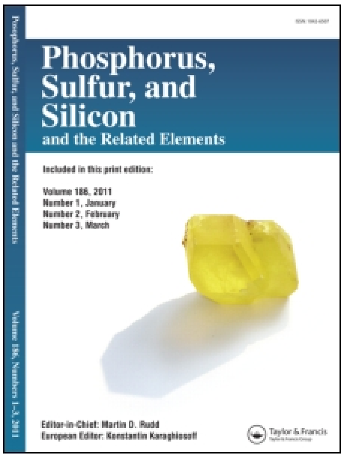

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PHOTOLYSIS OF DIPHOSPHONATE DERIVATIVES HAVING AROMATIC RING ASSEMBLIES

Min Shi[a]; Yoshiki Okamoto[a]; Setsuo Takamuku[a]
[a] The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, Japan

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PHOTOLYSIS OF DIPHOSPHONATE DERIVATIVES HAVING AROMATIC RING ASSEMBLIES

MIN SHI, YOSHIKI OKAMOTO,* and SETSUO TAKAMUKU
The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka, Japan 567

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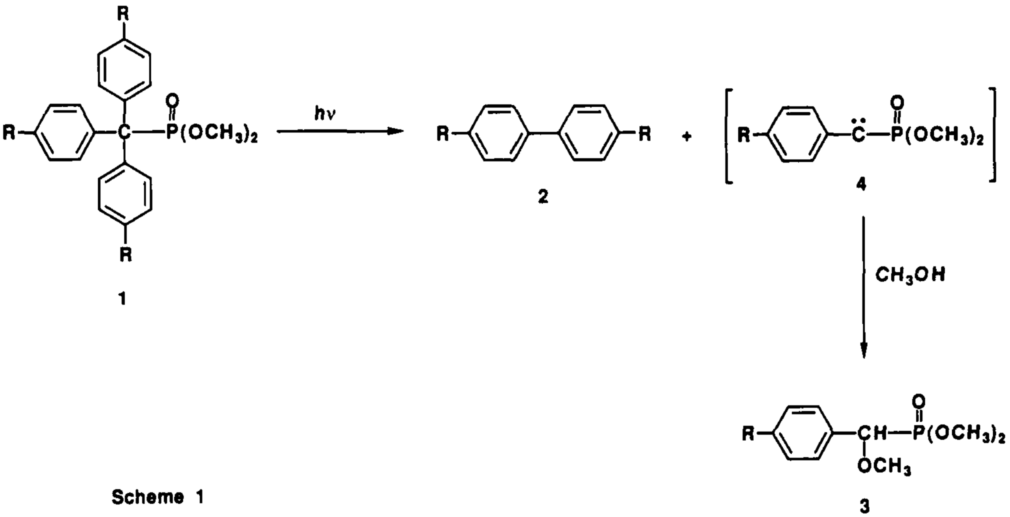
Upon UV-irradiation in methanol the diphosphonates fully substituted with aromatic rings give biaryls and aryl(dimethoxy) carbene derivatives in quantum yield of 0.01–0.03. The mechanism of the selective α,α-elimination of aryl groups was discussed.

Key words: Photolysis; α,α,α′,α′-Tetraaryl-α,α′-bis(dimethoxyphosphinyl)-*p*-xylene; bis[α,α-diphenyl-α-(dimethoxyphosphinyl)-*p*-tolyl]-methane; bis[α,α-diphenyl-α--(dimethoxyphosphinyl)-*p*-tolyl] ether; dimethyl [methoxy(aryl)methyl]phosphonate; dimethyl [*p*-biphenylyl(diphenyl)methyl]phosphonate; carbene generation

INTRODUCTION

Our recent studies on the photolysis of dimethyl triarylmethylphosphonate (**1**) in methanol have revealed that **1** undergoes selectively photochemical α,α-elimination of two aryl groups to afford biaryl (**2**) and dimethyl [methoxy(aryl)methyl]-phosphonate (**3**), which was derived from the insertion of the aryl(dimethoxy-phosphinyl)carbene intermediate (**4**) into the O—H bond of methanol, in the quantum yields of 0.01–0.02 (Scheme 1).[1] Therefore, this reaction is regarded as a novel generation of the carbene bearing a dimethoxyphosphinyl group. This finding prompted us further to study on the photolysis of other phosphonate de-



Scheme 1

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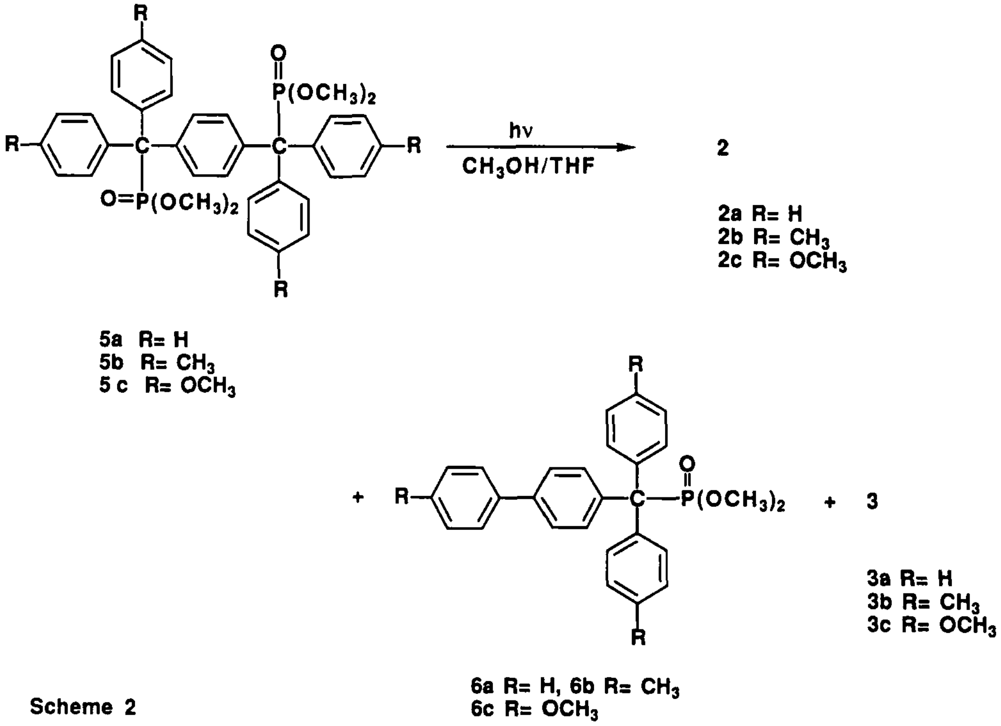
* The author to whom correspondence should be sent.

rivatives. In the present paper, we wish to report photolysis of diphosphonate derivatives having more aromatic ring assemblies (**5**). Through this study, the interaction of their aromatic rings will be revealed more closely. Moreover, the generation of the dicarbene intermediates bearing dimethoxyphosphinyl groups can be expected.

RESULTS AND DISCUSSION

Upon UV irradiation in methanol for 3 h, α,α,α′,α′-tetraphenyl-α,α′-bis(dimethoxyphosphinyl)-*p*-xylene (**5a**) not only gave dimethyl [methoxy(phenyl)methyl]-phosphonate (**3a**) but afforded dimethyl [*p*-biphenylyl(diphenyl)methyl]phosphonate (**6a**) in the yields of 41 and 42%, respectively. Biphenyl (**2a**) was given only in a yield of 2.5% (Scheme 2). The total quantum yield of **6a** and **2a** was 0.014. A dicarbene product, α,α′-bis(dimethoxyphosphinyl)-α,α′-bis(dimethoxy)-*p*-xylene, could not be obtained.

Previously, the formation of the carbene **4** as an intermediate in the photolysis of **1** had been postulated, which may be derived by photochemical α,α-elimination of the two aryl groups:[1] upon UV-irradiation the intramolecular charge transfer interaction among the three benzene rings of the triarylmethyl group arises and biaryl generates via the initial bonding between C-1 positions of two aryl groups (ipso coupling) followed by α,α-elimination. The similar photochemical generation of a carbene intermediate was proposed by Iwamura and Yoshimura[2] on photolysis of triptycene, as a special case of di-π-methane rearrangement,[3] in which the



Scheme 2

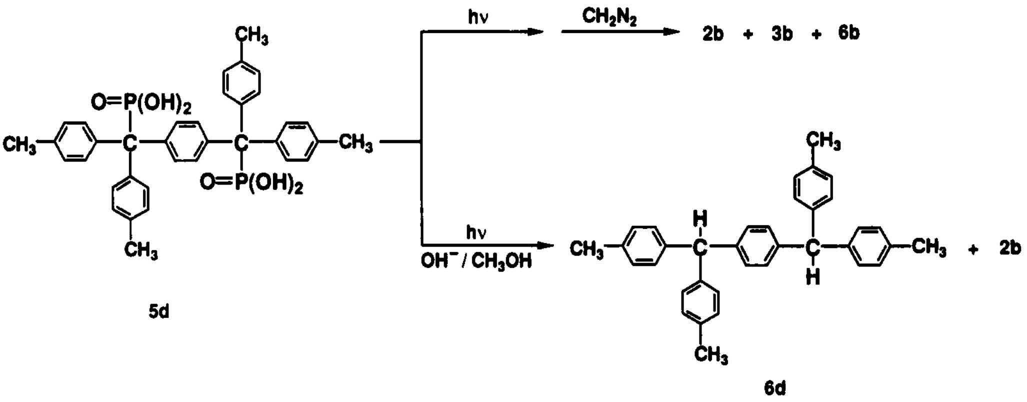
fragmentation occurs from biradical intermediates instead of cyclization to cyclopropane derivatives. In photolysis of tetraphenylmethane[4] and dibenzonorbornadiene,[5] the analogous carbene generation have been also reported. This photomolecular detachment of **2** may proceed via the excited singlet state (S_1).

In the present photolysis of **5a**, the similar mechanism can be presumed. The yield of **6a** (41%) was much larger than that of **2a** (2.5%). This result suggests that coupling between phenyl and 1,4-phenylene groups occurred overwhelmingly. In other words, a phenyl group may have much more interaction with 1,4-phenylene group than another phenyl group. In the previous paper, we have also reported that the inter-ring charge transfer interaction between the unsubstituted and substituted aromatic rings is much more than that between two unsubstituted aromatic rings.[1]

Terphenyl, which may be derived by further photolysis of **6a** could not be detected. In an attempt to gain a more certain edivence for this photochemical reactivity of **6a**, we have tried to photolyze **6a** itself, prepared by other methods as described below, and found that **6a** was quite stable for prolonged irradiation. Although the absorption spectrum of **1a** or **6a** look very similar, the latter has a larger molecular extinction coefficient compared with **1a** or **5a**, and its absorption band remained the intensity of absorption until 320 nm. Biphenylyl group must possess a lowest triplet state (T_1), so that an intramolecular energy transfer has occurred from the S_1 state localized on phenyl groups to the T_1 state localized on the biphenylyl group.[6]

We have further studied the photolysis of some *p*-substituted derivatives, α,α,α′,α′-tetra-*p*-tolyl-α,α′-bis(dimethoxyphosphinyl)-*p*-xylene (**5b**) and α,α,α′,α′-tetrakis-(4-methoxyphenyl)-α,α′-bis(dimethoxyphosphinyl)-*p*-xylene (**5c**) under the similar conditions, and obtained the similar results as that of **5a**. Dimethyl [methoxy(*p*-tolyl)methyl]phosphonate (**3b**) and dimethyl [methoxy(4-methoxyphenyl)methyl]phosphonate (**3c**) were given in the yields of 42 and 49%, respectively, for 3 h irradiation. These products (**3b** and **3c**) were derived from the insertion of the corresponding carbene intermediates (**4**), generated in this photolysis, into the O—H bond of methanol. Biaryl could not be obtained. The quantum yields of **3b** and **3c** were 0.017 and 0.020, respectively, which were slightly larger than that of **3a** in the unsubstituted derivatives **5a**. The counter product of **3b**, dimethyl [di-*p*-tolyl(*p*-tolylphenyl)-methyl]phosphonate (**6b**), also was obtained in a yield of 41%. But the counter product of **3c**, dimethyl [bis(4-methoxyphenyl)(4-methoxyphenyl-4′-phenyl)methyl]phosphonate (**6c**) could not be detected under the GLC analysis. These facts also suggest that by introducing a substituent in benzene ring, an inter-ring charge-transfer interaction between the benzene ring and the 1,4-phenylene ring may be so unaffected for the α,α-elimination.

We also examined the photochemical behavior of α,α,α′,α′-tetra(*p*-tolyl)-α,α′-bis(dihydroxyphosphinyl)-*p*-xylene(**5d**) in methanol and found that **5d** exhibited a different behavior from that of **5a-c**: increasing pH of the solution, the yields of dimethyl [methoxy(*p*-tolyl)methyl]phosphonate (**3b**) and **6b**, which were formed after treating with diazomethane (Scheme 3), decreased gradually as shown in Figure 1, and white precipitate also appeared. The precipitate was identified as α,α,α′,α′-tetra(*p*-tolyl)-*p*-xylene (**6d**), which was apparently derived from the C—P bond cleavage[1] and increased with the increase of pH (Scheme 3, Figure 1).



Scheme 3

On the other hand, we further prepared some interesting compounds such as **5e** and **5f**. They are dimmers of **1**, which are linked by a methylene group or oxygen atom at the phenyl groups of each other's. Upon UV irradiation in methanol under the same conditions as described above the major products were **3a**, dimethyl [4-

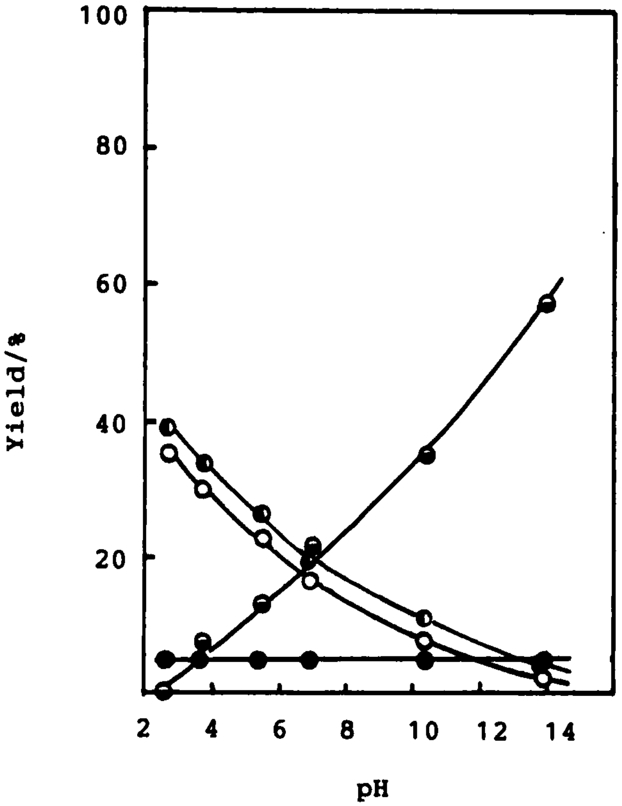


FIGURE 1 Effect of pH of photolysis of **5d** in 90% methanol solution (5.0×10^{-3} mol dm^{-3}) for 1 h. ● **2b**; ○ **3b**; ⊖ **6d**; ◐ **6b**.

(*p*-biphenylylmethyl)phenyl]diphenylmethylphosphonate (**6e**), and dimethyl [4-(*p*-biphenylyloxy)phenylmethylphosphonate (**6f**), and a trace amount of **2a** (Scheme 4). In these cases, the similar α,α-elimination of aryl groups as that of **5a** was also observed.

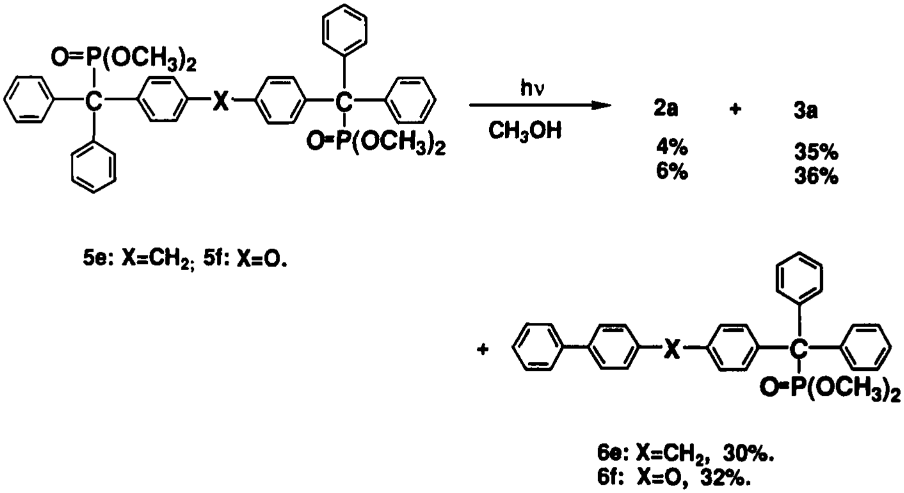
Geminal photochemical elimination of two aryl groups to give **3** has previously also been reported on other elements such as Zn,[7] Al,[8] B,[9] and Sn.[10]

EXPERIMENTAL

Mp and bp were obtained with a Yanagimoto Micro Melting Point Apparatus and were uncorrected. All of the compounds reported in this paper gave satisfactory CH microanalyses with a Perkin-Elmer Model 240 analyzer. UV-visible spectra were recorded with a Hitachi 150-20 spectrometer as MeOH solvent. ^{1}H NMR spectra were determined as a solution in $CDCl_3$ (unless otherwise stated) with tetramethylsilane (TMS) as an internal standard on a Bruker-AM360 spectrometer. IR spectra were taken as KBr disks using a Hitachi Model 345 spectrometer. GLC analyses were carried out using a 2% Silicone OV-17 on Chrom. WAW DMCS (60/80 mesh) with a Shimadzu Model 7A chromatography. GC-MS spectra were recorded with a JMS-DX300 instrument. Some authentic samples for GC were commercially available, and the others were prepared by the known method. The yields were determined using triphenylmethane as an internal reference.

Materials. *α,α,α′,α′-Tetraphenyl-α,α′-bis(dimethoxyphosphinyl)-p-xylene* (**5a**). **5a** was prepared by the reaction of α,α,α′,α′-tetraphenyl-α,α′-dichloro-*p*-xylene with trimethyl phosphite in benzene at refluxing for 2 h.[11] The crude product was recrystallized from benzene/hexane. mp 220–222 °C, UV_{max}(MeOH) 261 nm (ε 780), IR(KBr) 1220 cm^{-1} (P=O), ^{1}H NMR($CDCl_3$, TMS) δ = 3.46(12H, d, J_{HH} = 10.0 Hz, OCH_3), 6.7–7.6(24H, m, Ph). Found: C, 68.90; H, 5.80 $C_{36}H_{36}O_6P_2$: C, 69.00; H, 5.79; P, 9.89%.

α,α,α′,α′-Tetra-p-tolyl-α,α′-bis(dimethoxyphosphinyl)-p-xylene (**5b**). **5b** was prepared from α,α,α′,α′-tetra-*p*-tolyl-α,α′-dichloro-*p*-xylene in the similar manner as described above. mp 208–212 °C, UV_{max}(MeOH) 267 nm (ε 1200), IR(KBr) 1223 cm^{-1} (P=O), ^{1}H NMR($CDCl_3$, TMS) δ = 2.20(12H, s, CH_3), 3.46(12H, d, J_{HH} = 10.0 Hz), 6.6–7.4(20H, m, Ar). Found: C, 69.88; H, 6.44 $C_{40}H_{44}O_6P_2$: C, 70.30; H, 6.50; P, 9.07%.



Scheme 4

α,α,α′,α′-Tetrakis(4-methoxyphenyl)-α,α′-bis(dimethoxyphosphinyl)-p-xylene (**5c**). **5c** was prepared from α,α,α′,α′-tetrakis(4-methoxyphenyl)-α,α′-dichloro-*p*-xylene in the similar manner as described above. mp 280–282 °C, UV$_{max}$(MeOH) 277 nm (ε 1500), IR(KBr) 1220 cm^{-1} (P=O), ^{1}H NMR(CDCl$_3$, TMS) δ = 3.48(12H, d, J_{HH} = 10.0 Hz, POCH$_3$), 3.70(12H, s, OCH$_3$), 6.4–7.3(20H, m, Ar). Found: C, 64.66; H, 5.80 $C_{40}H_{44}O_{10}P_2$: C, 64.34; H, 5.94; P, 8.30%.

α,α,α′,α′-Tetra-p-tolyl-α,α′-bis(dihydroxyphosphinyl)-p-xylene (**5d**). **5d** was prepared by demethylation of **5d** with (CH$_3$)$_3$SiCl/LiBr/CH$_3$CN as follows: A mixture of **5b** (40 mmol) and (CH$_3$)$_3$SiCl(9.8 g, 90 mmol)/LiBr(7.8 g, 90 mmol) in acetonitrile was stirred at 60 °C for 5 h.[12] After cooling, the precipitate was filtered off and the solvent was evaporated. The residue was treated with CH$_3$OH to give the crude acid, which was recrystallized from 80% ethanol. mp 220–230 °C, UV$_{max}$(MeOH) 267 nm (ε 1200), IR(KBr) 3630 cm^{-1} (O—H), 1220 cm^{-1} (P=O), ^{1}H NMR(CH$_3$OD, TMS) δ = 2.20(12H, s, CH$_3$), 6.70–7.40(20H, m, Ar). Found: C, 68.79; H, 5.80 $C_{36}H_{36}P_2O_6$: C, 69.00; H, 5.79%.

Bis[(α,α-diphenyl-α-dimethoxyphosphinyl)-p-tolyl]methane (**5e**). **5e** was prepared from the reaction of bis[(α,α-diphenyl-α-chloro)-p-tolyl]methane[11] with trimethyl phosphite in the similar manner as described above. Oily compound, UV$_{max}$(MeOH) 270 nm (ε 1400), IR(Neat) 1222 cm^{-1} (P=O), ^{1}H NMR(CDCl$_3$, TMS) δ = 3.50(12H, d, J_{HH} = 8.0 Hz), 4.01(2H, s, CH$_2$), 7.0–7.60(28H, m, Ar). Found: C, 71.89; H, 6.01 $C_{43}H_{42}P_2O_6$: C, 72.06; H, 5.91%.

Bis[(α,α-diphenyl-α-dimethoxyphosphinyl)-p-tolyl] ether (**5f**). **5f** was prepared from the reaction of bis[(α,α-diphenyl-α-chloro)-*p*-tolyl] ether[11] with trimethyl phosphite in the similar manner as described above. mp 156–158 °C, UV$_{max}$(MeOH) 275 nm (ε 2300), IR(KBr) 1220 cm^{-1} (P=O), ^{1}H NMR(CDCl$_3$, TMS) δ = 3.60(12H, d, J_{HH} = 8.0 Hz), 7.0–7.60(28H, m, Ar). Found: C, 70.07; H, 5.72 $C_{42}H_{40}P_2O_7$: C, 70.19; H, 5.61%.

A General Procedure for Photolysis. a) A 3-ml MeOH solution of **5**, except **5d**, (1.0×10^{-2} mol dm^{-3}) was charged in a quartz tube (Φ = 10 mm) and purged of dissolved air by bubbling with argon gas. It was irradiated with a merry-go-round apparatus using an high pressure mercury lamp (300W) at ambient temperature. After irradiation of desired periods, the mixture was sampled for analysis of GLC. The yields of products and the conversions of **5** were determined using triphenylmethane as an internal standard. b) A 3-ml MeOH solution of **5d** (5.0×10^{-3} mol dm^{-3}) was adjusted at pH 14 with a 10% aqueous solution of NaOH, and irradiated in the same manner as described above.

Photolysis of 5b (in a Preparative Scale). A 300-ml MeOH solution of **5b** (1.0×10^{-2} mol dm^{-3}) was purged of dissolved air by bubbling with argon. It was irradiated in a quartz doughnut-type cell (10 mm thick) with a high pressure mercury lamp (300W) at ambient temperature for 3 h. After the solvent was removed under reduced pressure, the residue was chromatographed on silica gel using chloroform and hexane as eluants to give **3b** and **6b**, which were confirmed with their spectra data.

Preparation of Authentic Samples. Dimethyl [Methoxy(phenyl)methyl]phosphonate (**3a**). Dimethyl hydroxybenzylphosphonate was prepared by the reaction of benzaldehyde with dimethyl phosphonate in the presence of CsF,[13] and subsequently, it was methylated with dimethyl sulfate in alkaline media. After usual work-up, **3a** was obtained by vacuum distillation. (bp 109–110 °C/0.05 mmHg), IR(Neat) 1224 cm^{-1} (P=O), ^{1}H NMR δ = 3.25(3H, s, OMe), 3.50(3H, d, J_{PH} = 10 Hz, POCH$_3$),[14] 3.70(3H, d, J_{PH} = 10 Hz, POCH$_3$)[13] 5.38(1H, d, J_{PH} = 15 Hz, HCO), 6.2–7.8(5H, m, Ph). HRMS(EI) m/z 230.0704 (M$^+$), $C_{10}H_{15}PO_4$ requires 230.0708.

Dimethyl [Methoxy(p-tolyl)methyl]phosphonate (**3b**). The phosphonate (**3b**) was prepared by the similar manner as described above. bp 108–112 °C/0.05 mmHg, IR(Neat) 1222 cm^{-1} (P=O), ^{1}H NMR δ = 2.26(3H, s, Me), 3.24(3H, s, OMe), 3.50(3H, d, J_{PH} = 10 Hz, POCH$_3$), 3.71(3H, d, J_{PH} = 10 Hz, POCH$_3$), 5.37(1H, d, J_{PH} = 15 Hz, HCO), 6.0–7.9(4H, m, Ar). HRMS(EI) m/z 244.0862 (M$^+$), $C_{11}H_{17}PO_4$ requires 244.0864.

Dimethyl [Methoxy(4-methoxyphenyl)methyl]phosphonate (**3c**). The phosphonate (**3c**) was prepared by the similar manner as described above. bp 114–116 °C/0.05 mmHg, IR(Neat) 1220 cm^{-1} (P=O), ^{1}H NMR δ = 3.25(3H, s, OMe), 3.50(3H, d, J_{PH} = 10 Hz, POCH$_3$), 3.71(3H, d, J_{PH} = 10 Hz, POCH$_3$), 3.70(3H,s, OMe), 5.37(1H, d, J_{PH} = 15 Hz, HCO), 6.40–7.20(4H, m, Ar). HRMS(EI) m/z 260.0812 (M$^+$), $C_{11}H_{17}PO_5$ requires 260.0813.

Dimethyl [p-Biphenylyl(diphenyl)methyl]phosphonate (**6a**). **6a** was prepared in the similar manner as described in the preparation of **5a–c**. mp 123–124 °C, UVmax(MeOH) 258 nm (ε 23500 dm^3 mol^{-1}

cm^{-1}), IR(KBr) 1216 cm^{-1} (P=O), ^{1}H NMR δ = 3.48(6H, d, J_{HP} = 9.6 Hz, OMe), 6.8–7.2(19H, m, Ar). Found: C, 75.66; H, 6.05%. $C_{27}H_{26}PO_3$: C, 75.51; H, 6.10%.

Dimethyl [Di-p-tolyl(p-tolylphenyl)methyl]phosphonate (**6b**). mp 130–132°C, IR(KBr) 1220 cm^{-1} (P=O), ^{1}H NMR δ = 3.27(9H, s, Me), 3.46(6H, d, J_{HP} = 9.6 Hz, $POCH_3$), 6.71–7.50(16H, m, Ar). HRMS(EI) m/z 470.2008 (M$^+$), $C_{30}H_{31}PO_3$ requires 470.2010.

α,α,α′,α′-Tetra(p-tolyl)-p-xylene (**6d**). **6d** was prepared by the reduction of α,α,α′,α′-tetra(p-tolyl)-α,α′-dichloro-*p*-xylene with lithium aluminum hydride in ether. mp 156–158 °C, ^{1}H NMR δ = 2.20(12H, s, CH_3), 5.60(2H, s, —CH—), 6.7–7.60(24H, m, Ar). HRMS(EI) m/z 466.2655 (M$^+$), $C_{36}H_{34}$ requires 466.2659.

Dimethyl [4-(p-Biphenylylmethyl)phenyl]diphenylmethylphosphonate (**6e**). **6e** was prepared in the similar manner as described in the preparation of **5a–c**. Viscous oil, ^{1}H NMR δ = 3.46(6H, d, J_{HP} = 9.6 Hz, $POCH_3$), 4.0(2H, s, CH_2), 7.0–7.60(23H, m, Ar).

Measurement of the Quantum Yield. The quantum yields were determined on the base of generated **3** and **2**. A low-pressure mercury lamp (60 W) was used as a 254-nm radiation source. A 3-ml methanol solution of **5** (1.0 × 10^{-2} mol dm^{-3}) in a quartz cell (10 mm × 10 mm) was irradiated. As an actimometry a potassium trioxalatoferrate (III) solution was used.[15] The yields of the products were measured by GLC (Shimadzu GC-7A, Silicone OV-7, 2%, Support; Uniport HP, 1-m glass column). The photolyses were carried out at the conversions less than 5%.

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