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Photolysis of Diaryl Triphenylmethylphosphonates

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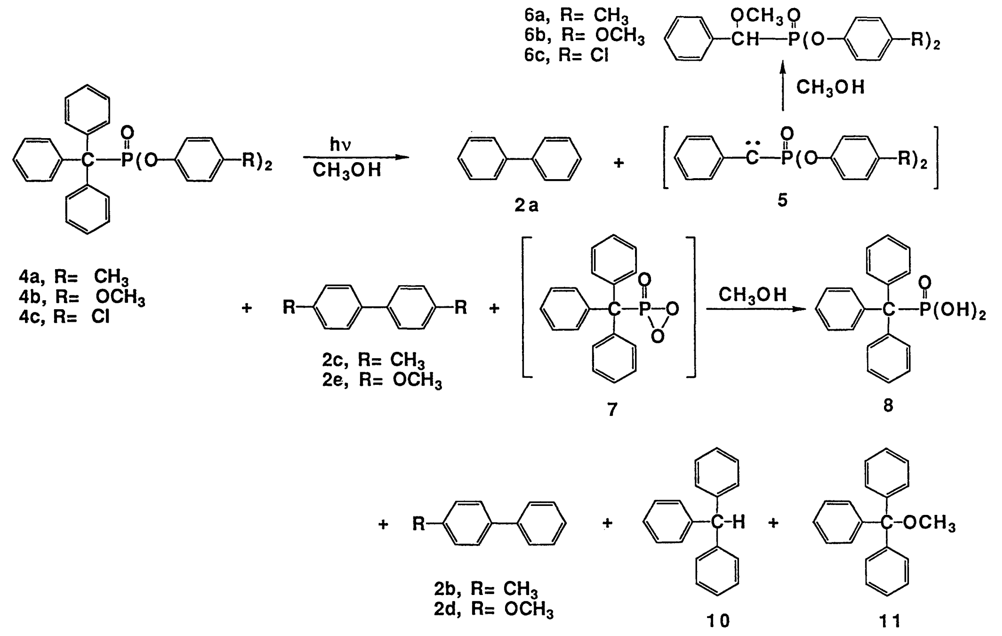
Synopsis. Upon UV irradiation in methanol, diaryl triphenylmethylphosphonate underwent three types of elimination of two aryl groups to give biaryls: the first is an α,α-elimination of two phenyl groups from a triphenylmethyl group which leads to the formation of the corresponding carbene intermediate; the second is an elimination of two aryl groups from a diaryl ester group to afford biaryl; the third is an elimination of phenyl and aryl groups from both moieties to give arylbenzene.

We have recently reported that upon UV irradiation in methanol, dimethyl triphenylmethylphosphonate (**1**) underwent an α,α-elimination of two phenyl groups to give biphenyl (**2a**) and the corresponding carbene intermediate, which inserted into the O-H bond of methanol to afford dimethyl α-methoxybenzylphosphonate.1) On the other hand, Finnegan and Matson reported that irradiation of an ethanol solution of triaryl phosphate (**3**) also provides biaryl (**2**) and some other products.2) This photochemical reaction was concluded as follows: the formation of **2** occurs intramolecularly either in a concerted fashion or between fragments very tightly contained within a solvent cage via an internal charge-transfer complex. These interesting results prompted us to investigate the photochemical behaviors of diaryl triphenylmethylphosphonates.

Results and Discussion

Upon UV irradiation in methanol, **4a** (R=CH_3) and **4b** (R=OCH_3) underwent three types of elimination of phenyls and/or aryls to give **2**: the first is the α,α-elimination of two phenyl groups from a triphenylmethyl group to afford **2a** and the corresponding carbene intermediate (**5**), which inserted into the O-H bond of methanol to provide the diaryl α-methoxybenzylphosphonate (**6**). The second is the elimination of two aryl groups from the ester group to give **2c** or **2e** and the "peroxidized" phosphorus species (**7**), which reacted with methanol to provide triphenylmethylphosphonic acid (**8**). The acid (**8**) was identified after converting to the corresponding dimethyl triphenylmethylphosphonate (**9**) by treatment with diazomethane. The third is the elimination of a phenyl from the triphenylmethyl group and an aryl group from the diaryl ester group, to give a cross coupling product of arylbenzene (**2b**, **2d**). However, in this case, the detection of the corresponding fragmented product failed. Triphenylmethane (**10**) and triphenyl(methoxy)methane (**11**), which were apparently derived from the C-P bond cleavage of **4a** or **4b**, were also obtained (Scheme 1). However, when bis(4-chlorophenyl) triphenylmethylphosphonate (**4c**, R=Cl) was irradiated under the similar conditions, only an α,α-elimination took place to provide **2a** and the corresponding carbene product. The finding that electron-withdrawing substituents such as chloro atom was unfavorable to the elimination of two aryl groups from the ester group has been also observed in the photolysis of **3**.2) Yields of the products were summarized in Table 1.

Concerning the further photochemical reactions of

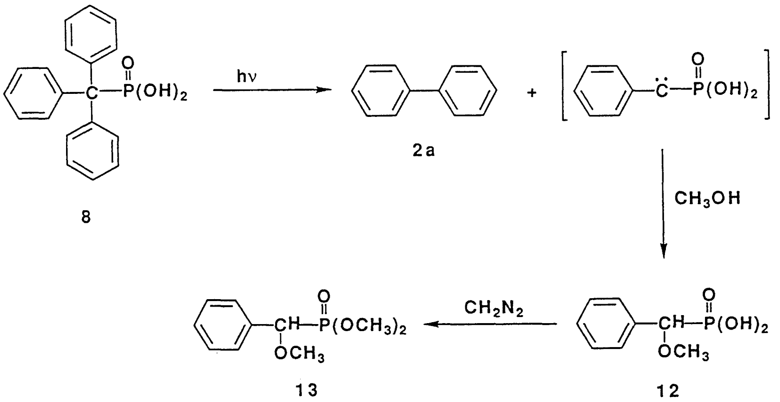


Scheme 1.

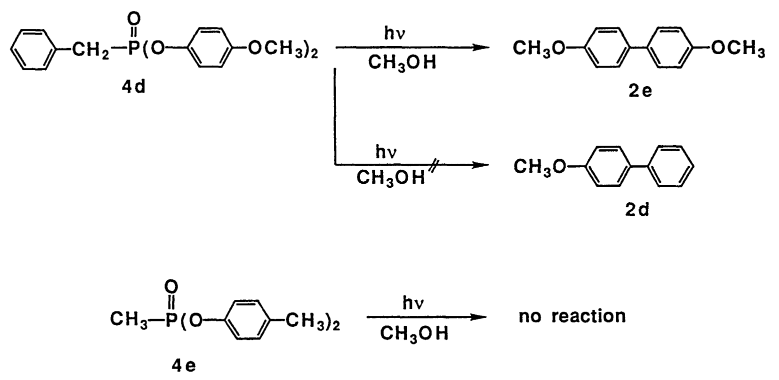
Table 1. Photolysis of **4** in Methanol[a)]

R	Conv./%	$\Phi^{b)}$	Product (yield/%)				
			2	**6**	**8**	**10**	**11**
CH_3	60	0.036	**2a**(27), **2b**(4), **2c**(14)	(14)	(Trace)	(Trace)	(4)
OCH_3	64	0.026	**2a**(4), **2d**(8), **2e**(16)	(1)	(Trace)	(Trace)	(20)
Cl	50	0.020	**2a**(18)	(16)	—	—	—

a) **4**: 1.0×10^{-2} mol dm^{-3}, irradiated in a quartz tube for 2 h. b) Total quantum yields of **2**.



Scheme 2.



Scheme 3.

the primary products, it should be noted that **8** also undergoes the photochemical α,α-elimination of two phenyl groups to give **2a** and α-methoxybenzylphosphonic acid (**12**), which was identified as dimethyl α-methoxybenzylphosphonate (**13**) after treating with an etheral solution of diazomethane.[1)] Therefore, the yield of **8** was extremely lower compared to that of the counter product **2c** or **2e** (Scheme 2). Among these photo-induced elimination of two aryl groups, the most surprising observation is the third elimination affording a cross coupled biaryl (**2b** or **2d**). In order to elucidate the mechanism of this novel elimination, we carried out the photolysis of bis(4-methoxyphenyl) benzylphosphonate (**4d**), and found that in methanol, only 4,4′-dimethoxybiphenyl (**2e**) could be detected by GLC but the formation of 4-methoxybiphenyl (**2d**) could not be confirmed (Scheme 3). The yield of carbene insertion product (**6b**) decreased by the further elimination of aryl groups to give **2e** in the same manner as the photolysis of **4d**. However, **6a** is very stable upon UV irradiation different from **6b**. We further checked the photochemical behavior of di-*p*-tolyl methylphosphonate (**4e**) and found that even upon a prolonged UV irradiation, no photolysis could be observed (Scheme 3).

These results indicate that both effects of steric configuration and electronic interaction may play very important roles in the formation of biaryls.

Experimental

Mps and bps were obtained with a Yanagimoto micro melting point apparatus and uncorrected. All of the compounds reported 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 $CDCl_3$ with tetramethylsilane (TMS) as an internal standard on a Bruker-AM360 spectrometer. IR spectra were determined as KBr disks using a Hitachi Model 345 spectrophotometer. 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 JMS-DX300 spectrometer. Some authentic samples were commercially available, and the others (**6**, **9**, **11**) were prepared by the known methods (see below). The yields were determined using methyl diphenylacetate as an internal reference.

General Procedure of Preparation of Diphenyl Triphenylmethylphosphonates (4a—4c). A toluene solution of triphenylmethylphosphonyl dichloride³⁾ (10 g, 27.7 mmol) and the corresponding phenol (110.8 mmol) was stirred for 10 h under refluxing. After cooling, the mixture was washed with a 30% sodium hydroxide aqueous solution and water. Then the crude product was purified by means of a flash-chromatography (eluant: hexane : chloroform=2 : 1).

Di-*p*-tolyl Triphenylmethylphosphonate (4a): (6.1 g, 43%), mp 182—184 °C, UV_{max}(MeOH) 267 nm (ε 1390 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1220 cm^{-1} (P=O), ^1H NMR δ=2.20 (6H, s, Me), 6.30—7.50 (23H, m, Ar). Found:C, 78.52; H, 5.76; P, 6.17%. Calcd for $C_{33}H_{29}PO_3$: C, 78.56; H, 5.79; P, 6.14%.

Bis(4-methoxyphenyl) Triphenylmethylphosphonate (4b): (7.2 g, 48%), mp 118—120 °C, UV_{max} (MeOH) 278 nm (ε 2000 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1218 cm^{-1} (P=O), ^1H NMR δ=3.62 (6H, s, OMe), 6.50—7.50 (23H, m, Ar). Found: C, 73.84; H, 5.43; P, 5.80%. Calcd for $C_{33}H_{29}PO_5$: C, 73.87; H, 5.45; P, 5.77%.

Bis(4-chlorophenyl) Triphenylmethylphosphonate (4c): (6.5 g, 43%), mp 160—162 °C, UV_{max}(MeOH) 262 nm (ε 1400 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1210 cm^{-1} (P=O), ^1H NMR δ=6.40—7.30 (m, Ar). Found: C, 68.23; H, 4.23; P, 5.70%. Calcd for $C_{31}H_{23}PO_3Cl_2$: C, 68.27; H, 4.25; P, 5.68%.

Bis(4-methoxyphenyl) Benzylphosphonate (4d): 4d was prepared by the reaction of benzylphosphonyl dichloride with 3 equivalent amounts of 4-methoxyphenol at 140 °C. After cooling, the reaction mixture was washed with a 30% aqueous sodium hydroxide solution and water. Then the crude product was purified by means of a flash-chromatography (eluant: hexane : chloroform=1 : 1) to afford a colorless oil. UV_{max}(MeOH) 280 nm (ε 3550 $dm^3 mol^{-1} cm^{-1}$), IR(neat) 1214 cm^{-1} (P=O), ^1H NMR δ=3.35 (2H, d, J_{PH}=20 Hz, $-CH_2-$), 3.63 (6H, s, OMe), 6.30—7.30 (13H, m, Ar).

Di-*p*-tolyl Benzylphosphonate (4e): UV_{max}(MeOH) 268 nm (ε 1300 $dm^3 mol^{-1} cm^{-1}$) , IR(neat) 1210 cm^{-1} (P=O), ^1H NMR δ=1.65 (3H, d, J_{PH}=18 Hz, Me), 2.20 (6H, s, Me), 6.40—7.30 (8H, m, Ar).

Preparation of Authentic Samples. Di-*p*-tolyl α-Methoxybenzylphosphonate (6a): Di-*p*-tolyl α-hydroxybenzylphosphonate was prepared by the reaction of benzaldehyde with di(*p*-tolyl) phosphonate in the presence of CsF,⁴⁾ and subsequent methylation with dimethyl sulfate in alkaline media. After usual work-up, the crude product was purified by use of a column chromatography (SiO_2) (eluant: hexane: chloroform=1 : 4) to yield pure **6a**. ^1H NMR δ=2.20 (6H, s, Me), 3.25 (3H, s, OMe), 5.40 (1H, d, J_{PH}=15 Hz, HCO), 6.30—7.60 (13H, m, Ar).

Bis(4-methoxyphenyl) α-Methoxybenzylphosphonate (6b): 6b was prepared in the same manner as described above. ^1H NMR δ=3.25 (3H, s, OMe), 3.64 (6H, s, OMe), 5.37 (1H, d, J_{PH}=15 Hz, HCO), 6.50—7.60 (13H, m, Ar).

Bis(A-chlorophenyl) α-Methoxybenzylphosphonate (6c): 6c was prepared in the same manner as described above. ^1H NMR δ=3.26 (3H, s, OMe), 5.40 (1H, d, J_{PH}=15 Hz, HCO), 6.30—7.60 (13H, m, Ar).

Dimethyl Triphenylmethylphosphonate (9): 9 was prepared by the method as previous.¹⁾ Mp 155—157 °C, IR(KBr) 1216 cm^{-1} (P=O), ^1H NMR δ=3.40 (6H, d, J_{PH}=9.6 Hz, OMe), 7.02 (15H, s, Ar). Found: C, 72.00; H, 5.88%. Calcd for $C_{21}H_{21}PO_3$: C, 71.58; H, 6.00%.

Methoxy(triphenyl)methane (11): 11 was prepared by the reaction of triphenylmethyl chloride with methanol and triethylamine in benzene.⁵⁾ After the triethylammonium chloride was filtered off, the solvent was removed from the filtrate by use of a rotary evaporator. The residue was purified by column chromatography (SiO_2) to afford **11** as a colorless oil. ^1H NMR δ=3.08 (3H, s, Me), 6.60—7.60 (15H, m, Ar).

Dimethyl α-Methoxybenzylphosphonate (13): 13 was prepared by the reaction of benzaldehyde with dimethyl phosphonate in the presence of CsF.⁴⁾ ^1H NMR δ=3.25 (3H, s, OMe), 3.50 (3H, d, J_{PH}=10 Hz, POMe),⁵⁾ 3.70 (3H, d, J_{PH}=10 Hz, POMe), 5.38 (1H, d, J_{PH}=15 Hz, HCO), 6.2—7.8 (5H, m, Ar).

A General Procedure of Photolysis. A 3-ml MeOH solution of **4** (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 a high pressure mercury lamp (300 W) 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 authentic samples. The product yields were determined by means of GLC calibration with methyl diphenylacetate as an internal standard.

Measurement of the Quantum Yield. The quantum yields were measured on the base of generated **2** in the same manner as reported previously.¹⁾

References

1) M. Shi, Y. Okamoto, and S. Takamuku, *J. Chem. Soc., Chem. Commun.*, **1989**, 151; M. Shi, Y. Okamoto, and S. Takamuku, *Bull. Chem. Soc. Jpn.*, **63**, 453 (1990).

2) R. A. Finnegan and J. A. Matson, *J. Am. Chem. Soc.*, **94**, 4780 (1972).

3) G. M. Kosolapoff, "The Synthesis of Phosphonic and Phosphinic Acids," in "Org. Reactions Vol. VI," ed by R. Adams, John Wiley & Sons Inc., New York (1957), p. 290.

4) F. T-Boullet and A. Foucaud, *Synthesis*, **1982**, 165.

5) M. F. Hawthorne and D. J. Gram, *J. Am. Chem. Soc.*, **76**, 3451 (1954).

6) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker (1973), p. 119.