Photolysis of Triarylmethylphosphonic Acids and Their Esters

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Upon UV-irradiation in an alkaline alcohol solution, some triarylmethylphosphonic acids underwent C-P bond cleavage to give triarylmethanes and alkyl dihydrogenphosphates, while, in an acidic or a neutral alcohol solution, they afforded biaryls. Their dimethyl esters gave also biaryls and dimethyl [alkoxy(aryl)methyl]phosphonates, which were derived from the insertion of (dialkoxyphosphinyl)arylcarbenes into the OH bond of the alcohol. The carbene was generated by photo-α,α-elimination of two aryl groups of the phosphonate.

The C-P bond of alkylphosphonic acid is generally stable either vigorously acidic or basic hydrolysis conditions.[1] Recently, the dephosphorylation of alkylphosphonic acid attracts much interest in connection with metabolism of naturally occurring alkylphosphonic acids and detoxification of herbicides, insecticides, and antibiotics that contain the phosphonic acid moiety.[2]

Previously, we have reported on photo-dephosphorylation of *p*-nitrobenzylphosphonic acid in alkaline alcohol solution.[3] The mechanism has been offered: the radical anion produced by photo-intramolecular electron transfer from the phosphono group to the nitrophenyl moiety undergoes homolytic C-P bond cleavage to give *p*-nitrobenzyl anion and monomeric metaphosphate anion, followed by the reaction with alcohol to afford *p*-nitrotoluene and alkyl dihydrogenphosphate, respectively.[4] The mechanism has received much attention owing to the similarity to that of photo-decarboxylation of *p*-nitrophenylacetate.[5]

In the course of these studies, we have discovered that upon irradiation in alkaline media, triphenylmethylphosphonic acid (**1a**), despite the absence of an electron-withdrawing substituent, gave also triphenylmethane (**2a**) and orthophosphate in a high yield. Furthermore, in acidic or neutral solution, surprisingly, **1a** gave biphenyl (**3a**) without C-P bond cleavage.[6] In this report, we report the results of photolysis of triarylmethylphosphonic acids (**1**) and its esters (**4**).

Results and Discussion

Photolysis of Triarylmethylphosphonic Acid (1). Upon irradiation in an alkaline ethanol solution, **1a** underwent C-P bond cleavage to afford **2a** and ethyl dihydrogenphosphate in a high efficiency of a quantum yield of 0.41.

The absorption spectra of the transient intermediate was observed by a flash photolysis of **1a** in alkaline aqueous solution (pH 12), as shown in Fig. 1.

This spectra having an absorption band at 450 nm may be assigned to triphenylmethyl anion,[7] which decayed at the first order rate constant of 1.0×10^{-2} s^{-1}.

Therefore, the photolysis of the dianion of **1a** may proceed in the similar way as that of the dianion of *p*-nitrobenzylphosphonic acid (Scheme 1).[4]

However in acidic or neutral media, **1a** exhibited a different photochemical behavior; lowering pH of the solution, the yield of **2a** decreased, while the yield of

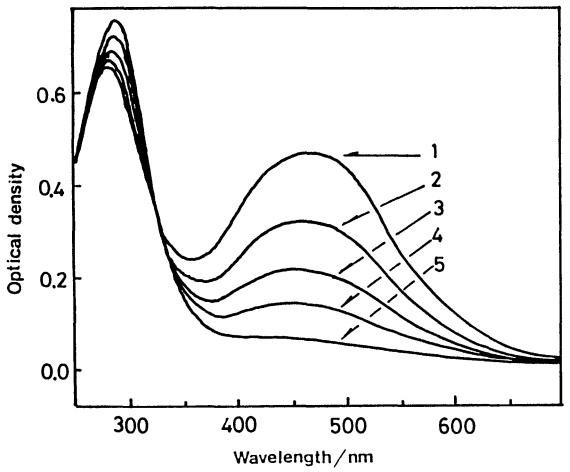
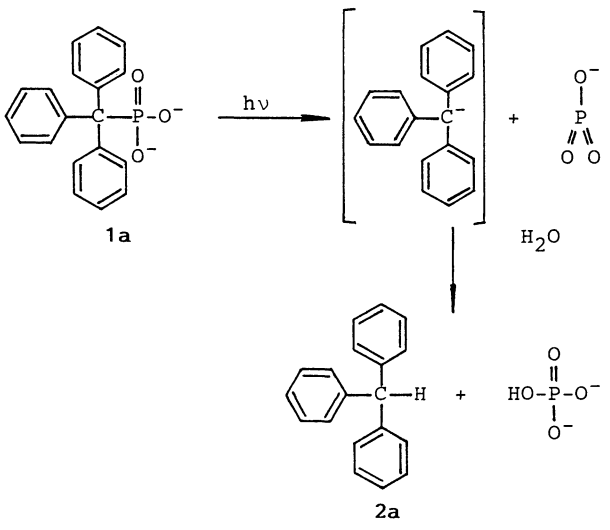


Fig. 1. Time-dependent absorption spectra obtained by Xe flash photolysis of **1a** in water (2.0×10^{-4} mol dm^{-3}, pH 12). Each trace, represents each spectrum at regular time intervals (10 s) after photolysis.



Scheme 1.

3a increased gradually as shown in Fig. 2.

Below pH 3, only **3a** was obtained in a yield of 22% (quantum yield 0.012), as a result of direct GLC-analysis of the irradiated solution. In order to search the other products than **3a**, after the irradiation, the methanol solution was treated with diazomethane. The results of GLC analysis revealed the formation of dimethyl α-methoxybenzylphosphonate (**5a**) in a yield of 19%.

These facts are formulated in Scheme 2.

In order to study further this photochemical behavior, photolysis of the other phosphonic acids (**1a—1f**) bearing a variety of substituents were investigated.

Table 1 shows the yields of **2a—2f** and **3a—3e** on the photolysis of **1a—1f** under the conditions of acidic or basic media.

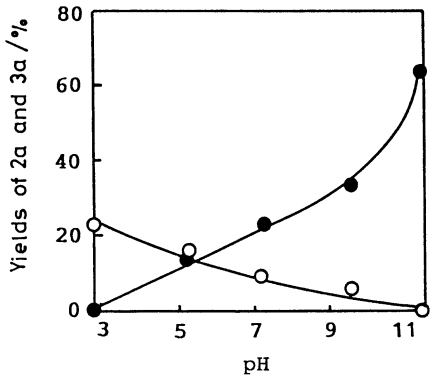


Fig. 2. Effect of pH of photolysis of **1a** in 90% methanol solution (1.0×10^{-2} mol dm^{-3}) for 2 h.
● **2a**; ○ **3a**.

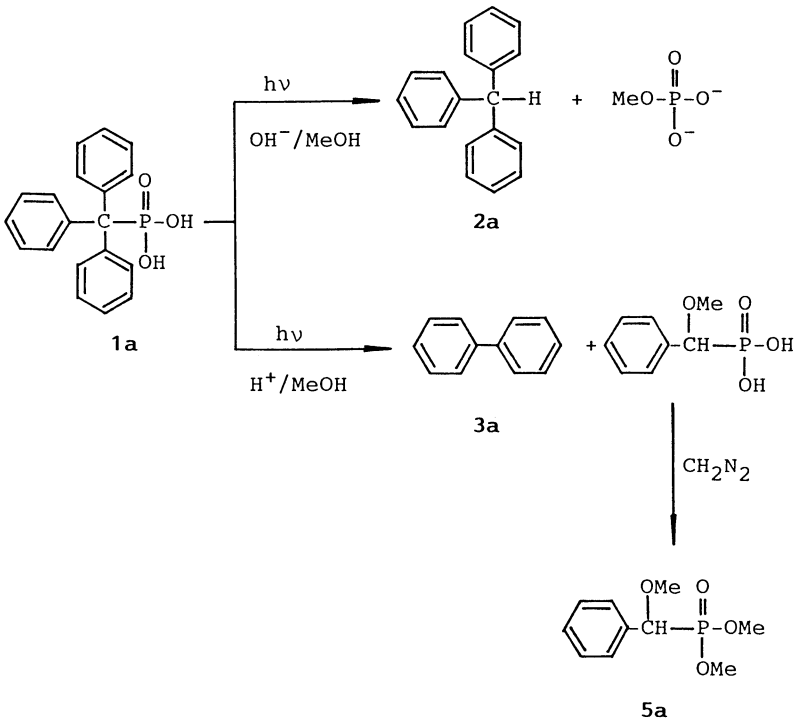
The acid (**1b**) having nitro groups gave only **2b** in alkaline media (pH 10), but in acidic media **1b** was unreactive for prolonged irradiation. The yields of triarylmethane (**2**) from the acids (**1d—1f**) bearing methoxyl groups were depressed, but in acidic media, the formations of biaryls (**3**) were facilitated, that is, the introduction of an electron-donating group, such as methoxyl group is proved to be effective for formation of **3**, regardless of pH of the solution. However, the increase of number of methoxyl group introduced gives no additional effects on their reactivities. On the other hand, the C-P bond cleavage was facilitated by the introduction of an electron-withdrawing substituent, because the triarylmethyl anion intermediate may be more stabilized by such substituents.

Photolysis of Dialkyl Triarylmethylphosphonates (4). The photolyses of **4a—4k** were carried out in methanol. The compound **4a** gave not only **3a** but dimethyl α-methoxybenzylphosphonate (**5a**) in a comparable yield, which was confirmed by comparison with GLC data of an authentic sample prepared by the other method.

Figure 3 illustrates the yields of **3a** and **5a**, and the conversion of **4a** as a function of irradiation time.

The rate of formation of **3a** was almost the same as that of **5a**, which increased linearly with the lapse of irradiation time until the conversion less than 30%. The conversion of **4a** reached 60% after 3 h-irradiation and their yields reached to 30% (the yield on the basis of the conversion was about 60%). The ratio of the products (**3a**/**5a**) did not change up to the conversion of 50%.

In ethanol, the formations of **3a** (29%) and dimethyl



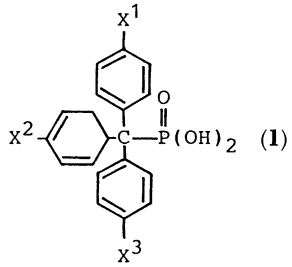
Scheme 2.

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

	1[b)]			pH[c)]	Product/Yield (%)	
	X^1	X^2	X^3		2	3
1a	H	H	H	3	Ph_3CH (**2a**) (0.0)	Ph_2 (**3a**) (22)
				10	**2a** (40)	**3a** (3.0)
1b	NO_2	NO_2	NO_2	3	$(NO_2C_6H_4)_3CH$ (**2b**) (0.0)	$(NO_2C_6H_4)_2$ (**3b**) (0.0)
				10	**2b** (52)	**3b** (0.0)
1c	Me	Me	Me	3	$(MeC_6H_4)_3CH$ (**2c**) (0.0)	$(MeC_6H_4)_2$ (**3c**) (25)
				10	**2c** (38)	**3c** (4.2)
1d	H	H	MeO	3	$(MeOC_6H_4)Ph_2CH$ (**2d**) (2.0)	**3a** (20) $MeOC_6H_4Ph$ (**3d**) (31)
				10	**2d** (6.0)	**3a** (19) **3d** (30)
1e	H	MeO	MeO	3	$(MeOC_6H_4)_2PhCH$ (**2e**) (0.0)	**3d** (7.5) $(MeOC_6H_4)_2$ (**3e**) (24)
				10	**2e** (6.0)	**3d** (7.0) **3e** (25)
1f	MeO	MeO	MeO	3	$(MeOC_6H_4)_3CH$ (**2f**) (0.0)	**3e** (30)
				10	**2f** (5.0)	**3e** (33)

a) The photolysis was carried out in methanol solutions of **1** (10^{-2} mol dm^{-3}) at ambient temperature for 2 h.

b)



(**1**)

c) pH's of the solutions were adjusted with aqueous 2 M NaOH or 1 M HCl solutions (1 M=1 mol dm^{-3}).

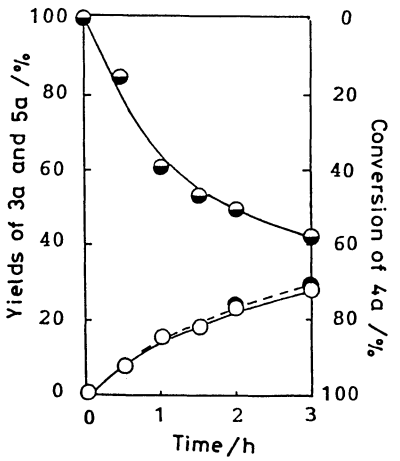


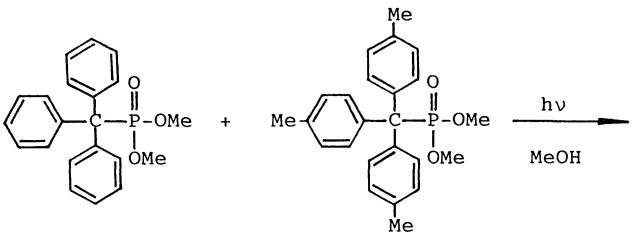
Fig. 3. The yields of **3a** and **5a**, and the conversion of **4a** as a function of irradiation time. Photolysis was carried out in methanol (1.0×10^{-2} mol dm^{-3}). ○ yield of **3a**; ● yield of **5a**; ◒ conversion of **4a**.

α-ethoxybenzylphosphonate (27%) were observed as similar as that in methanol.

Irradiation of dimethyl [(4-methylphenyl)diphenylmethyl]phosphonate (**4b**) in a methanol solution, also gave **3a** and 4-methylbiphenyl (**3f**) in 11 and 24% yield, respectively. And the corresponding two kinds of dimethyl [methoxy(aryl)methyl]phosphonates; **5a** and dimethyl [methoxy(4-methylphenyl)methyl]phosphonate (**5b**) were obtained in yields of 23 and 10%, respectively.

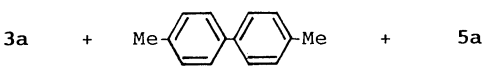
Photolysis of dimethyl [tris(4-methylphenyl)methyl]phosphonate (**4d**) in methanol gave also 4,4′-dimethylbiphenyl (**3c**) and **5b** in yields of 45 and 43%, respectively.

The photolysis of a mixture of two kinds of the



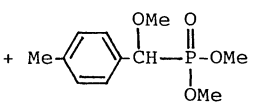
4a **4d**

1 : 1



3c

1 : 4

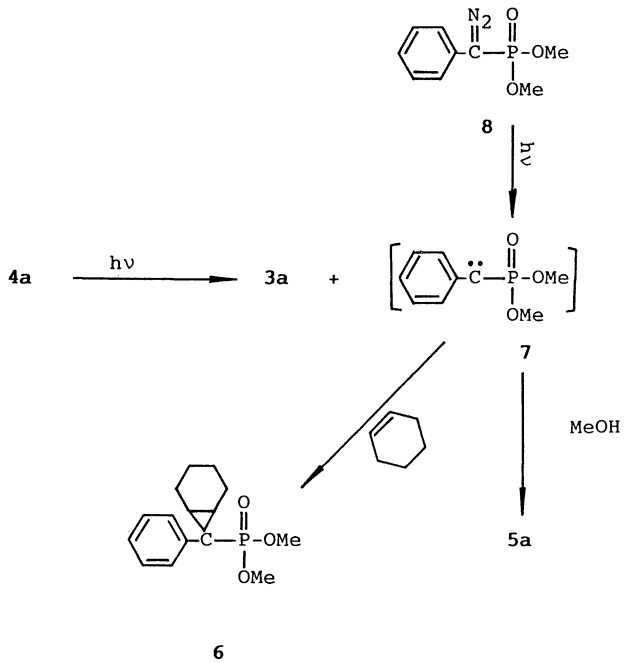


(1)

5b

phosphonates **4** was carried out; an equimolar mixture of **4a** and **4d** in methanol gave **3a** and **3c** at the ratio of 4:1. An intermolecular crossed product, **3f** could not be detected (Eq. 1). The fact that a crossed product **3f** is absent suggests that the reaction proceeds in a manner of intramolecular elimination, namely, a molecular detachment of **3** or simultaneous elimination of two aryl groups from one molecule of **4**.

In other solvents, such as diethyl ether or acetonitrile, photolysis of **4a** also proceeds in the similar manner to give **3a**, although the detection of the other products derived from the reaction with the solvent was failed. The photolysis of **4a** in cyclohexene gave **3a** and dimethyl (7-phenyl-7-norcaryl)phosphonate (**6**) (as a 1:1 mixture of syn and anti isomers), derived from addition of the carbene (**7**) to the double bond of the olefin.[8] The photolysis of dimethyl (α-diazobenzyl)phosphonate (**8**) in ethanol or cyclohexene was carried out under the same conditions, and the same product **5a** or **6** was obtained, respectively (Scheme 3).[9]



Scheme 3.

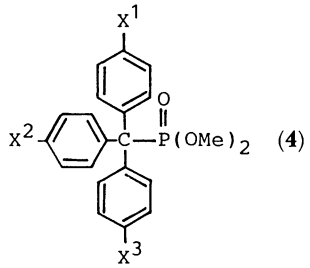
The similarities of both results lead to further corroborating evidence for this postulate. Therefore, the formation of carbene **7** as an intermediate can be postulated, which may be derived from **4a** by photochemical α,α-elimination of two aryl groups. Two phenyl groups are photo-eliminated via the initial bonding between C-1 positions of two phenyl groups (ipso coupling). The resulting carbene **7** either inserted to OH bond of the alcohol or added to the C-C double bond of the cyclohexene to give these products, respectively. Hence, what we want to emphas-

Table 2. Photolysis of **4** in Methanol[a]

	4[b]			Φ[c]	Conv. %	Product (3, yield/%)			
	X¹	X²	X³			A[d]		B[d]	
4a	H	H	H	0.012	44	**3a**	(22)	—	
4b	H	H	Me	0.013	61	**3a**	(11)	MeC_6H_4Ph (**3f**)	(24)
4c	H	Me	Me	0.015	50	**3c**	(18)	**3f**	(29)
4d	Me	Me	Me	0.018	60	**3c**	(45)	—	
4e	H	H	OMe	0.031	60	**3a**	(17)	**3d**	(27)
4f	H	OMe	OMe	0.027	50	**3e**	(10)	**3d**	(30)
4g	OMe	OMe	OMe	0.036	—[e]	**3e**	(40)	—	
4h	H	H	F	0.021	70	**3a**	(15)	FC_6H_4Ph (**3g**)	(27)
4i	H	H	Cl	0.020	46	**3a**	(6)	ClC_6H_4Ph (**3h**)	(32)
4j	H	Cl	Cl	0.019	50	$(ClC_6H_5)_2$ (**3i**)	(17)	**3h**	(15)
4k	H	Me	Cl	0.020	64	—		**3b**	(8)
								3h	(13)
								MeC_6H_4Ph (**3j**)	(13)

a) The photolysis was carried out in methanol solutions of **4** (10^{-2} mol dm^{-3}) at ambient temperature for 2 h.

b)



(**4**)

c) Quantum yield based on the combined yields of all **3** produced.

d) **A**=symmetry **3**, **B**=unsymmetry **3**.

e) **4g** could not be analyzed by GLC, because of the thermal instability.

ize is a novel photochemical generation of carbene.

The product arising from the hydrogen abstraction by the carbene could not be detected, and even in the presence of molecular oxygen, the yields of **3a** and **5a** were almost unchanged, consequently, we presume that the photo-molecular detachment of biphenyl proceed from the excited singlet state with a short lifetime. Photolysis of dimethyl [(biphenylyl)diphenylmethyl]phosphonate (**4l**) and dimethyl (1-naphthyldiphenylmethyl)phosphonate (**4m**) gave only a trace amount of **3a**, respectively. Dimethyl [(4-bromophenyl)diphenylmethyl]phosphonate (**4n**) gave a photo-debrominated product, **4a**, (64%) and **3a** (6.0%). The latter may be derived from the former.

In an attempt to gain more insight in the underlying mechanism responsible for the α,α-elimination of two aryl groups, we have further studied the photolysis of some *p*-substituted derivatives **4b—4k** under the similar conditions. The quantum yields of **3** and the selectivities of the α,α-elimination of aryl groups were determined (Table 2).

In general, the quantum yields of **3** from the substituted derivatives **4b—4k** were larger than that of **3a** from the unsubstituted derivatives **4a**.

The introduction of substituent, regardless electron-donating or electron-withdrawing properties, enhances the elimination of **3**, and the reactivities of monosubstituted phosphonates **4b**, **4e**, **4h**, and **4i** may be subject to apparent substituent effect in the order of MeO, F, Cl, Me, and H. For example, a quantum yield of **3** from **4e** was much more than that from **4a**. These facts suggest that the increasing of an inter-ring charge-transfer interaction between the benzene ring and the substituted benzene ring may be effective for the α,α-elimination of two aryl groups.

However, the ratios (A/B) of eliminations of symmetrical and unsymmetrical **3** from mono- or disubstituted **4** (**4b**, **4c**, **4e**, **4f**, **4h**, **4i**, and **4j**) did not so much deviate from the value (2.0) expected if the groups coupled randomly, except for the case of monochloroderivatives (**4i** and **4k**).

Consequently, the formation of the carbene as an intermediate can be postulated as in Scheme 4.

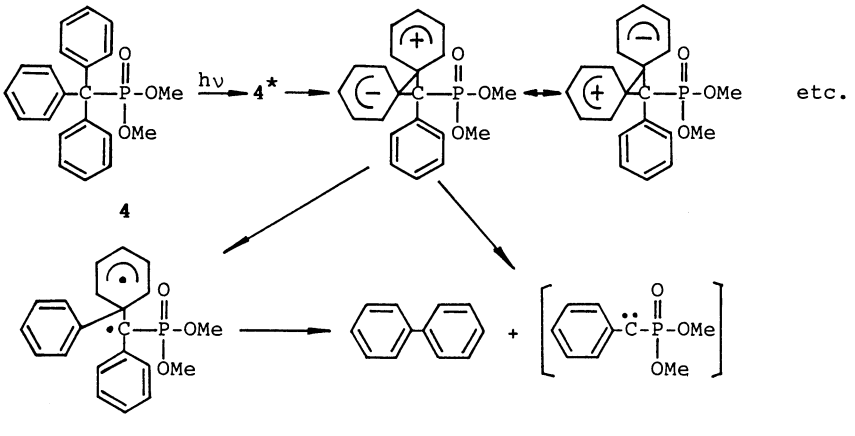
In a photo-excited state of this acid, probably, singlet excited state (**4***), the intramolecular charge-transfer interaction among the three phenyl rings occurred, and subsequently, two phenyl groups are eliminated via the initial bonding between C-1 positions of two phenyl groups (ipso coupling). The elimination of biphenyl may proceed in stepwise or concerted wise. The mechanism of this reaction is understood in terms of photochemical di-π-methane rearreangement. Then, the carbene intermediate (**7**) was formed, followed by conversion into final products by the reaction with solvent, i.e., insertion into the OH-bond of alcohol or addition to the double bond of cyclohexene.

Similar intramolecular charge-transfer interaction was also observed among the three benzene rings of triptycene derivatives, where the similar photochemical generation of a carbene intermediate was proposed by Iwamura and Yoshimura,[10] as a special case of di-π-methane rearrangement,[11] in which the fragmentation occurs from biradical intermediates instead of cyclization to cyclopropane derivatives. In photolysis of tetraphenylmethane[12] and dibenzonorbornadiene,[13] the analogous carbene generation have been also reported. In the present reaction, a similar reaction mechanism can be presumed.

Geminal photochemical elimination of two aryl groups to give **3** has been reported on other elements such as Zn,[14] Al,[15] B,[16] and Sn.[17]

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. Transient absorption spectra were measured by a spectro multichannel photodetector, MCPD-100 (Ostuka Electronic Co., Ltd.). ^{1}H NMR spectra were determined as a solution in $CDCl_3$ (unless otherwise stated) with tetra-



Scheme 4.

methylsilane (TMS) as an internal standard on a Bruker-AM360 spectrometer. IR spectra were taken as KBr disks using a Hitachi Model 345. GLC analyses were carried out using a 2% Silicone OV-17 on Chrom. WAW DMCS (60/80 mesh) with a Shimadzu Model 7A. GC-MS spectra were recorded with a JMS-DX300. Some authentic samples for GC were commercially available, and the others (**5a** and **5b**) were prepared by the known method (see below). The yields were determined using **2a** or **3a** as internal references.

Preparation of (Triphenylmethyl)phosphonic Acid (1a). **1a** was prepared by the reaction of triphenylmethanol with PCl_3 (50%),[18] mp 284—287 °C, UV_{max}(MeOH) 260 nm (ε 560 $dm^3 mol^{-1} cm^{-1}$), IR (KBr) 2850 cm^{-1} (OH); ^1H NMR δ=6.42 (2H, br, OH), 7.20 (15H, m, Ar). Found: C, 70.46; H, 5.11; P, 9.38%. Calcd for $C_{19}H_{17}PO_3$: C, 70.37; H, 5.28; P, 9.55%.

[Tris(4-nitrophenyl)methyl]phosphonic Acid (1b): The nitration of **1a** (3.2 g, 10 mmol) was carried out with fuming HNO_3 (50 ml) below 0 °C.[3] After nitration, the mixture was poured on ice. The volatile acid was expelled as completely as possible with bubbling of nitrogen gas. The solution was concentrated in vacuo as possible and permitted to stand at room temperature overnight. The crude product was recrystallized from water (4.2 g, 75%). Mp 298—300 °C, UV_{max}(MeOH) 293 nm (ε 44000 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 2850 cm^{-1} (OH), ^1H NMR (D_2O, DSS, NaOD, pH 12) δ=7.83 (6H, d, J_{HH}=8.4 Hz, Ar), 8.22 (6H, d, Ar). Found: C, 49.27; H, 3.15; N, 9.03; P, 6.49%. Calcd for $C_{19}H_{14}N_3PO_9$: C, 49.68; H, 3.07; N, 9.15; P, 6.74%.

Preparation of Other Triarylmethylphosphonic Acids (1c—1f). The corresponding diesters (**4d—4g**) were subjected to demethylation by the reaction with Me_3SiCl/LiBr/CH_3CN as follows: General procedure: A mixture of **4** (40 mmol) and a mixture of Me_3SiCl (9.8 g, 90 mmol) and LiBr (7.8 g, 90 mmol) in acetonitrile (50 ml) was stirred at 60 °C for 5 h.[19] After cooling, the precipitates were filtered off and the solvent was evaporated. The residue was treated with MeOH to give the crude acid, which was recrystallized from 80% EtOH.

[Tris(4-methylphenyl)methyl]phosphonic Acid (1c): (11.7 g, 80%), mp 294—297 °C, UV_{max}(MeOH) 268 nm (ε 969 $dm^3 mol^{-1} cm^{-1}$), ^1H NMR δ=2.20 (9H, s, CH_3), 6.60 (2H, br, OH), 6.72 (12H, s, Ph). Found: C, 72.39; H, 6.25; P, 8.29%. Calcd for $C_{22}H_{23}PO_3$: C, 72.12; H, 6.32; P, 8.45%.

[(4-Methoxyphenyl)diphenylmethyl]phosphonic Acid (1d): (11.3 g, 80%), mp 277—280 °C, UV_{max}(MeOH) 271 nm (ε 4560 $dm^3 mol^{-1} cm^{-1}$), ^1H NMR δ=3.75 (3H, s, CH_3O), 7.00—7.40 (14H, m, Ar). Found: C, 67.56; H, 5.11; P, 8.54%. Calcd for $C_{20}H_{19}PO_4$: C, 67.79; H, 5.40; P, 8.74%.

[Bis(4-methoxyphenyl)phenylmethyl]phosphonic Acid (1e): (11.2 g, 73%), mp 250—251 °C, UV_{max}(MeOH) 277 nm (ε 3340 $dm^3 mol^{-1} cm^{-1}$), ^1H NMR δ=3.74 (6H, s, CH_3O), 7.02—7.39 (13H, m, Ar). Found: C, 65.16; H, 5.52; P, 8.31%. Calcd for $C_{21}H_{21}PO_5$: C, 65.62; H, 5.51; P, 8.06%.

[Tris(4-methoxyphenyl)methyl]phosphonic Acid (1f): (13.0 g, 78%), mp 270—271 °C, UV_{max}(MeOH) 278 nm (ε 4550 $dm^3 mol^{-1} cm^{-1}$), ^1H NMR δ=3.72 (9H, s, CH_3O), 7.28—7.31 (12H, m, Ar). Found: C, 62.62; H, 5.72; P, 7.20%. Calcd for $C_{22}H_{23}PO_6$: C, 63.77; H, 5.60; P, 7.48%.

General Procedure of Preparation of Dimethyl (Triarylmethyl)phosphonates (4a—4n). A benzene solution of triarylmethyl chloride (30 mmol) was added into trimethyl phosphite (90 mmol) under refluxing temperature for 2 h. The mixture was cooled to 0 °C, and the precipitates were recrystallized from MeOH.

Dimethyl (Triphenylmethyl)phosphonate (4a): (8.5 g, 80%), mp 155—157 °C, UV_{max}(MeOH) 260 nm (ε 677 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1261 cm^{-1} (P=O), ^1H NMR δ=3.40 (6H, d, J_{HP}=9.6 Hz, OMe), 7.02 (15H, s, Ph). Found: C, 72.00; H, 5.88%. Calcd for $C_{21}H_{21}PO_3$: C, 71.58; H, 6.00%.

Dimethyl [(4-Methylphenyl)diphenylmethyl]phosphonate (4b): (8.8 g, 80%), mp 118—121 °C, UV_{max}(MeOH) 264 nm (ε 710 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1220 cm^{-1} (P=O), ^1H NMR δ=2.25 (3H, s, CH_3), 3.50 (6H, d, J_{HP}=9.6 Hz, OMe), 6.70—7.30 (14H, m, Ar). Found: C, 72.24; H, 6.40. Calcd for $C_{22}H_{23}PO_3$: C, 72.12; H, 6.33%.

Dimethyl [Bis(4-methylphenyl)phenylmethyl]phosphonate (4c): (9.1 g, 80%), mp 122—124 °C. UV_{max} (MeOH) 266 nm (ε 734 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1220 cm^{-1} (P=O); ^1H NMR δ=2.30 (3H, s CH_3), 3.50 (6H, d, J_{HP}=9.6 Hz, OMe), 6.70—7.30 (13H, m, Ar). Found: C, 72.39; H, 6.49%. Calcd for $C_{23}H_{25}PO_3$: C, 72.62; H, 6.62%.

Dimethyl [Tris(4-methylphenyl)methyl]phosphonate (4d): (9.7 g, 82%), mp 148—150 °C, UV_{max}(MeOH) 267 nm (ε 932 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1220 cm^{-1} (P=O), ^1H NMR δ=2.28 (9H, s, CH_3), 3.48 (6H, d, J_{HP}=9.6 Hz, OMe), 7.0 (12H, s, Ar). Found: C, 72.85; H, 6.63%. Calcd for $C_{24}H_{27}PO_3$: C, 73.08; H, 6.90%.

Dimethyl [(4-Methoxyphenyl)diphenylmethyl]phosphonate (4e): (9.8 g, 85%), mp 125—130 °C, UV_{max}(MeOH) 268 nm (ε 2450 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1218 cm^{-1} (P=O), ^1H NMR δ=3.50 (6H, d, J_{HP}=10.4 Hz, OMe), 3.70 (3H, s, OMe), 6.50—7.80 (14H, m, Ar). Found: C, 69.23; H, 6.18%. Calcd for $C_{22}H_{23}PO_4$: C, 69.10; H, 6.06%.

Dimethyl [Bis(4-methoxyphenyl)phenylmethyl]phosphonate (4f): (10.5 g, 85%), mp 142—145 °C, UV_{max}(MeOH) 277 nm (ε 3210 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1218 cm^{-1} (P=O), ^1H NMR δ=3.45 (6H, d, J_{HP}=9.6 Hz, OMe), 3.70 (6H, s, OMe), 6.40—7.60 (13H, m, Ar). Found: C, 66.40; H, 6.02; P, 7.37%. Calcd for $C_{23}H_{25}PO_5$: C, 66.98; H, 6.11; P, 7.51%.

Dimethyl [Tris(4-methoxyphenyl)methyl]phosphonate (4g): (11.9 g, 90%), mp 162—165 °C, UV_{max}(MeOH) 276 nm (ε 3900 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1218 cm^{-1} (P=O); ^1H NMR δ=3.58 (6H, d, J_{HP}=9.6 Hz, OMe), 3.78 (9H, s, OCH_3), 6.50—7.60 (12H, m, Ar). Found: C, 65.23, H, 6.23; P, 7.27%. Calcd for $C_{24}H_{27}PO_6$: C, 65.15; H, 6.15; P, 7.00%.

Dimethyl [(4-Fluorophenyl)diphenylmethyl]phosphonate (4h): (10.1 g, 90%), mp 143—147 °C, UV_{max}(MeOH) 260 nm (ε 1060 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1216 cm^{-1} (P=O), ^1H NMR δ=3.48 (6H, d, J_{HP}=9.6 Hz, OMe), 6.0—7.4 (13H, m Ar). Found: C, 67.43; H, 5.38%. Calcd for $C_{21}H_{20}FPO_3$: C, 68.10; H, 5.44%.

Dimethyl [(4-Chlorophenyl)diphenylmethyl]phosphonate (4i): (10.4 g, 90%), mp 135—138 °C, UV_{max}(MeOH) 260 nm (ε 1500 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1216 cm^{-1} (P=O), ^1H NMR δ=3.50 (6H, d, J_{HP}=9.6 Hz, OMe), 7.04 (14H, s, Ar). Found: C, 64.90; H, 5.04%. Calcd for $C_{21}H_{20}ClPO_3$: C, 65.21; H, 5.21%.

Dimethyl [Bis(4-chlorophenyl)phenylmethyl]phosphonate (4j): (11.3 g, 80%), mp 153—156 °C, UV_{max}(MeOH) 261 nm (ε 1280 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1216 cm^{-1} (P=O), ^1H NMR δ=3.50 (6H, d, J_{HP}=9.6 Hz, OMe), 7.0—7.2 (13H, m, Ar). Found: C, 59.35; H, 4.20%. Calcd for $C_{21}H_{19}Cl_2PO_3$: C, 59.87; H, 4.55%.

Dimethyl [(4-Chlorophenyl)(4-methylphenyl)phenylmethyl]phosphonate (4k): (7.2 g, 60%), mp 138—140 °C. UV_{max}(MeOH) 270 nm (ε 1000 $dm^3 mol^{-1} cm^{-1}$), IR(KBr)

1217 cm^{-1} (P=O), ^1H NMR δ=2.25 (3H, s, CH_3), 3.50 (6H, J_{HP}=9.6 Hz, OMe), 6.7—7.3 (13H, m, Ar). Found: C, 65.70; H, 4.76%. Calcd for $C_{22}H_{22}ClPO_3$: C, 65.92; H, 5.53%.

Dimethyl [(4-Biphenylyl)diphenylmethyl]phosphonate (4l): (8.5 g, 70%), mp 123—124 °C, UV_{max}(MeOH) 258 nm (ε 23500 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1216 cm^{-1} (P=O), ^1H 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 [1-Naphthyldiphenylmethyl]phosphonate (4m): (9.7 g, 80%), mp 173—176 °C, UV_{max}(MeOH) 283 nm (ε 5040 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1216 cm^{-1} (P=O), ^1H NMR δ=3.32 (6H, d, J_{HP}=9.6 Hz, OMe), 6.4—8.2 (17H, m, Ar). Found: C, 74.08; H, 5.11%. Calcd for $C_{25}H_{23}PO_3$: C, 74.62; H, 5.76%.

Dimethyl [(4-Bromophenyl)diphenylmethyl]phosphonate (4n): (8.5 g, 80%), mp 124—126 °C, UV_{max}(MeOH) 260 nm (ε 1900 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1216 cm^{-1} (P=O), ^1H NMR δ=3.45 (6H, d, J_{HP}=9.6 Hz, OMe), 6.4—7.4 (14H, m, Ar). Found: C, 58.77; H, 4.72%. Calcd for $C_{21}H_{20}BrPO_3$: C, 58.48; H, 4.67%.

Diethyl Triphenylmethylphosphonate (7a): A benzene solution of triarylmethyl chloride (30 mmol) was added into triethyl phosphite (90 mmol) under refluxing temperature for 2 h. The mixture was cooled to 0 °C, and the precipitate was recrystallized from MeOH. (6.8 g, 60%), mp 120—122 °C, UV_{max}(MeOH) 260 nm (ε 644 $dm^3 mol^{-1} cm^{-1}$), IR(KBr) 1219 cm^{-1} (P=O); ^1H NMR δ=1.05 (6H, t, CH_3), 3.82 (4H, d-q, J_{HH}=7.0 Hz, J_{HP}=6.4 Hz OCH_2), 7.10 (15H, s, Ph). Found: C, 72.58; H, 6.61%. Calcd for $C_{23}H_{25}PO_3$: C, 72.61; H, 6.62%.

Preparation of Authentic Samples. Dimethyl α-Methoxybenzylphosphonate (5a): The phosphonate (**5a**) was prepared by the reaction of benzaldehyde with dimethyl phosphonate in the presence of CsF,[20] and subsequently, it was methylated with dimethyl sulfate. After usual work-up, **5a** was obtained by vacuum distillation (bp 109—110 °C/0.05 mmHg; 1mmHg≈133.322 Pa). ^1H NMR δ=3.25 (3H, s, OMe), 3.50 (3H, d, J_{PH}=10 Hz, POMe),[21] 3.70 (3H, d, J_{PH}=10 Hz, POMe), [21] 5.38 (1H, d, J_{PH}=15 Hz, HCO), 6.2—7.8 (5H, m, Ph).

Dimethyl [Methoxy(4-methylphenyl)methyl]phosphonate (5b). The phosphonate (**5b**) was prepared by the similar manner as described above. (Bp 108—112 °C/0.05 mmHg), ^1H NMR δ=2.26 (3H, s, Me), 3.24 (3H, s, OMe), 3.50 (3H, d, J_{PH}=10 Hz, POMe), 3.71 (3H, d, J_{PH}=10 Hz, POMe), 5.37 (1H, d, J_{PH}=15 Hz, HCO), 6.0—7.9 (4H, m, Ar).

A General Procedure for Photolysis. A 3-ml MeOH solution of **1** or **4** (1.0×10^{-2} mol dm^{-3}) was charged in a quartz tube (if in alkaline media, the solution was adjusted at prescribed pH with 10% aqueous NaOH) and purged of dissolved air by bubbling with argon gas. It was irradiated in a quartz tube (ϕ=10 mm) 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 yields of **2** and **3** were determined using methyl diphenylacetate as an internal standard. On the other hand, the yield and conversion of **3** and **4** were determined using **2a** as an internal standard.

In the case of using EtOH as a solvent, the similar result was obtained.

The photolyses of **4a** in other solvents, cyclohexene, acetonitrile, and diethyl ether were also carried out in the similar manner as described above. In all cases, the yields of **3a** were almost the same, although the corresponding products arising from the carbene could not be detected with GLC analysis, except in the case using cyclohexene as a solvent. The 1 : 1 adduct of the carbene and cyclohexene was determined by comparison with the GLC data of authentic samples, prepared as mentioned below.

Photolysis of a Mixture of 4a and 4d. A 3-ml of MeOH solution of equimolar mixture of **4a** and **4d** (0.5×10^{-2} mol dm^{-3}, respectively) was irradiated for 3 h in the similar manner as described above. The products **3a**, **3c**, **5a**, and **5b** were obtained in yields of 12, 49, 11, and 47%, respectively. The product **3f** could not be detected.

Photolysis of 4a in the Presence of Molecular Oxygen. Three 3-ml MeOH solutions of **4a** (1.0×10^{-2} mol dm^{-3}) were charged in quartz tubes (ϕ=10 mm) separately. Argon, air or oxygen was bubbled into the solutions at 20 °C for 10 min, respectively, and they were irradiated at the same time, with a merry-go-round apparatus, in the similar manner as described above. In these cases, the yields of **3a** were almost unchanged.

Photolysis of 1a (in a Preparative Scale). In acidic media; a 100 ml MeOH solution of **1a** (1.0×10^{-2} mol dm^{-3}, pH 3.1) was purged of dissolved air by bubbling with argon gas. It was irradiated in a quartz doughnut-type cell (10 mm thick) with a high pressure mercury lamp (300 W) at ambient temperature for 3 h. After the solvent was evaporated, the residue was extracted with benzene. The benzene phase was washed with aqueous NaOH (10%), H_2O and dried ($MgSO_4$). Concentration gave an almost pure product (**3a**), which was confirmed with the spectral data of an authentic sample, after recrystallization from benzen.

b) In alkaline media; a 100-ml MeOH solution of **1a** (1.0×10^{-2} mol dm^{-3}) was adjusted at pH 12 with a 10% aqueous solution of NaOH, and irradiated in the similar manner as described above. After the similar work-up, almost pure **2a** was obtained, which was confirmed with the spectral data of an authentic sample.

Photolysis of 4a (in a Preparative Scale). A 100-ml MeOH solution of **4a** (1.0×10^{-2} mol dm^{-3}) was irradiated in the similar manner as described above. After the solvent was removed off, the residue was chromatographed on silica gel using benzene and $CHCl_3$ as eluents to give **3a** and **5a**, which were confirmed with the spectral data of authentic samples.

Photolysis of Dimethyl α-Diazobenzylphosphonate (8). The phosphonate (**8**) was prepared by the known method.[8] A 100-ml MeOH solution of **8** (20 mol dm^{-3}) was irradiated in a quartz tube with a high-pressure mercury lamp for 20 min. The product was isolated by vacuum distillation (bp 109—110 °C/0.05 mmHg). This product was also used for comparison with the products obtained in photolysis of **4a**.

Photolysis of **8** in cyclohexene (10 mmol dm^{-3}) was also carried out in similar manner as described above.[8]

Two 1 : 1-adducts of cyclohexene and the carbene (**6**) were obtained as the results of GC-MS (m/z=280), which may be syn and anti-isomers (total yield 51%). These products were the same as the products obtained in photolysis of **4a** in cyclohexene. The similar result was also reported on the photolysis of methyl aryldiazoacetate.[22]

Flash Photolysis. An aqueous solution of **1a** (2.0×10^{-4} mol dm^{-3}) was put in a quartz cell (10 mm×10 mm) equipped a long tube with a seal septum. It was deoxygen-

ated by bubbling with Ar. Flash photolysis was carried out by using a Xe-pulse lamp (50 s) at ambient temperature. The transmission of the sample was monitored using a MCPD.

Measurement of the Quantum Yield. The quantum yields were measured on the bases of generated **2a** or **3**. A low-pressure mercury lamp (60 W) with a Vicor glass filter was used as the 254-nm radiation source. A 3-ml methanol solution of **4** or **1a** (5.0×10^{-3} mol dm^{-3}) in a quartz cell (10 mm×10 mm) was irradiated (in the case of **1a**, the pH of the solution was adjusted to 12 with 10% NaOH aqueous solution). As an actinometry a potassium trioxalatoferrate(III) solution was used.[23] The yields of the products were measured by GLC (Shimadzu GC-7A, Silicone OV-7, 2%, Support; Uniport HP, 1-m glass column, **2a** or **3a** was used as an internal standard). The photolyses were carried out at the conversions less than 5%.

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