# Photolysis of Triphenylmethylphosphonic Acid and its Dimethyl Esters: A Novel Photochemical Generation of Dimethoxyphosphinyl(phenyl)carbene by α,α-Elimination of Phenyl Groups

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Photolysis of triphenylmethylphosphonic acid and its dimethyl ester in ethanol gave biphenyl and a product derived from dimethoxyphosphinyl(phenyl)carbene.

Upon u.v. irradiation in alkaline aqueous solution, *p*-nitrobenzylphosphonic acid (**1**) underwent C–P bond cleavage to give *p*-nitrotoluene and orthophosphate (quantum yield, Ø = 0.80).[1] This photochemical C–P bond cleavage occurs only in a fully dissociated state. In acidic solution (**1**) is stable even upon prolonged irradiation.[2] However, in the absence of base, triphenylmethylphosphonic acid (**2a**)† and its dimethyl ester (**2b**)† exhibited different photochemical behaviour from that

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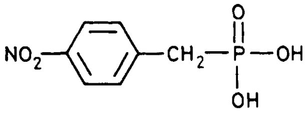
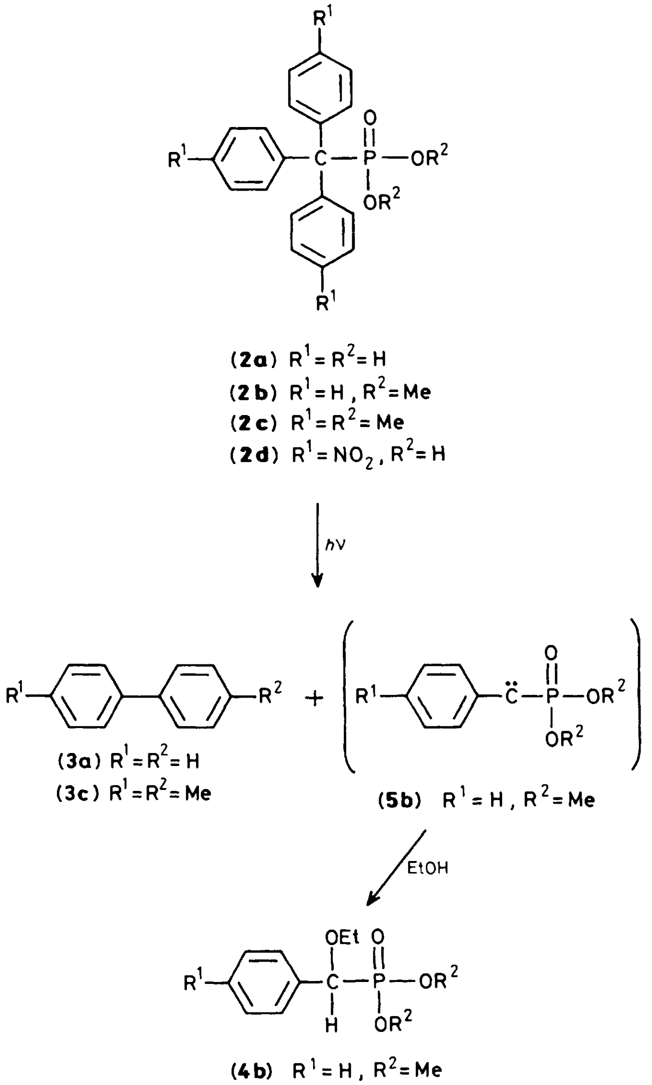
† Spectral data for (**2a**),[3] (**2b**),[4] (**2c**),[4] and (**2d**);[4] $\lambda_{max}$ (EtOH) ($\varepsilon$/dm$^{-3}$ mol$^{-1}$ cm$^{-1}$) 260 (340), 260 (680), 267 (930), and 283 (8900) nm, respectively.



(1)



**Scheme 1.** *Reagents and conditions*; (2) ($1.0 \times 10^{-2}$ mol dm$^{-3}$) in 95% EtOH, in a quartz tube, was irradiated with a high pressure mercury lamp (300 W) under argon atmosphere at ambient temperature.

of (**1**); according to g.c. analysis of the reaction mixture, the photolysis of (**2a**) in ethanol in an argon atmosphere afforded only biphenyl (**3a**). The photolysis of (**2b**) in ethanol gave (**3a**) and dimethyl 1-ethoxybenzylphosphonate (**4b**)‡ as an additional product (Scheme 1). The product (**4b**) may be derived from dimethoxyphosphinyl(phenyl)carbene (**5b**), generated photochemically by α,α-elimination of aryl groups from (**2b**), which underwent insertion into the OH bond of ethanol. After irradiation for 3 h, the products (**3a**) and (**4b**) were formed simultaneously with 30 and 29% yields, respectively. The rates of formation of (**3a**) from (**2b**) in ethanol were almost the same as that of (**2a**). The presence of oxygen did not affect the yield of (**3a**), but (**4b**) was not formed.

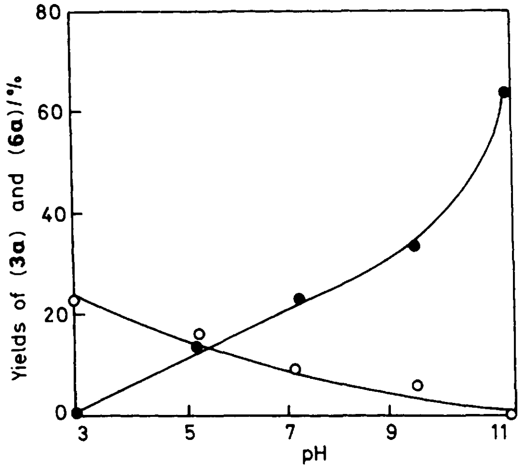
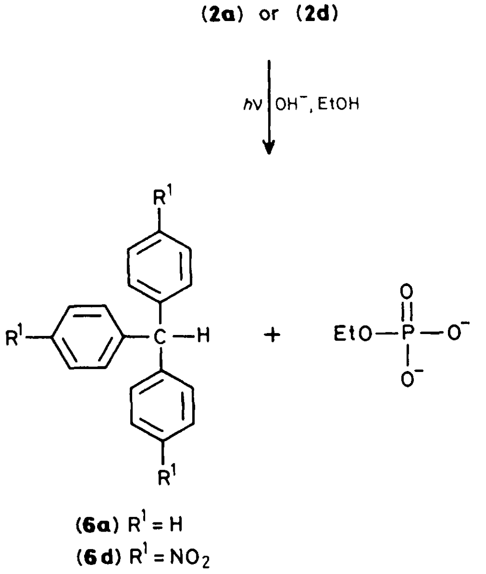


**Figure 1.** Effect of pH on yields of (**3a**) and (**6a**). Irradiation conditions; 90% ethanol solution of (**2a**) ($1.0 \times 10^{-2}$ mol dm$^{-3}$) for 2 h. ○ yield of (**3a**); ● yield of (**6a**).



**Scheme 2.** *Reagents and conditions*; (**2b**) or (**2d**) ($1.0 \times 10^{-2}$ mol dm$^{-3}$) in 90% EtOH, adjusted at pH 12 with 10% aq. NaOH, in a quartz tube was irradiated as for Scheme 1.

In other solvents, such as diethyl ether, acetonitrile, and cyclohexene, photolysis of (**2b**) gave (**3a**) in the same yields. In cyclohexene, the product‡ derived from the addition of carbene (**5b**) to the double bond was obtained.

On increasing the pH of the solution of (**2a**), the yield of triphenylmethane (**6a**) increased, while the yield of (**3a**) decreased gradually as shown in Figure 1. In alkaline solution (above pH 11) only (**6a**) was obtained (Scheme 2). The photolysis of the dianion of (**2b**) may proceed in a similar way to that of the dianion (**1**).[2] The phosphonate (**2c**)† also gave 4,4′-dimethylbiphenyl (**3c**). The photolysis of an equimolar mixture of (**2b**) and (**2c**) gave a mixture of (**3a**) and (**3c**) in the

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‡ These products were identified by the comparison of g.c., mass, and $^1$H and $^{31}$P n.m.r. spectral data with data for authentic samples obtained by the photolysis of dimethyl α-diazobenzylphosphonate in ethanol[5] and cyclohexene.[6]

ratio 1:4. The absence of the cross product, 4-methylbiphenyl, indicated the unimolecular and simultaneous elimination of the two phenyl groups: *i.e.*, molecular detachment of biphenyl. Therefore, emphasis should be given to the novel photochemical generation of carbene. Geminal photoelimination of two aryl groups to give a biaryl is known for other elements, boron[7] and tin[8], but, to the best of our knowledge, not yet for carbon. However, the formation of a carbene intermediate in the photolysis of triptycene may be significant.[9] This photolytic reactivity of (**2**) may be subject to an apparent substituent effect; the order of reactivities was (**2c**) > (**2a**), (**2b**) > (**2d**).† The acid (**2d**) hardly underwent such a photolysis in acid, whereas in basic media, (**2d**) was highly photosensitive and decomposed into tris(4-nitrophenyl)-methane (**6d**) and an orthophosphate derivative (Scheme 2).

*Received, 26th July 1988; Com. 8/03052I*

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