The Temperature Dependence of Product Distributions in the Photolysis of α-Diazobenzylphosphonates in Alcohols [1]
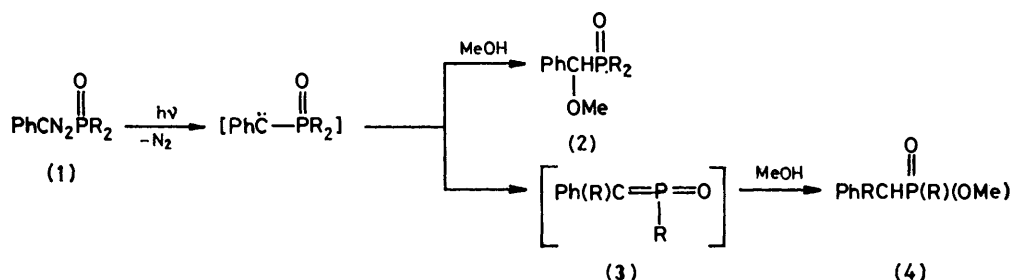
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The product distributions from the photolysis of α-diazobenzylphosphonates (1) in alcohols change dramatically with the temperature used. Thus the direct photolysis of (1) in alcohols at 27 °C gives the O–H insertion product, whereas in frozen alcohol matrices at −196 °C it resulted in the C–H insertion products in high yield. Photolysis of (1) in alcohol at 27 °C, sensitized by Michler's ketone, leads to a significant increase in the yield of double hydrogen-abstraction product as well as the C–H insertion products. The C–H insertion products in the matrix experiments are explained in terms of hydrogen abstraction of triplet phosphorylcarbene, followed by efficient recombination of the resulting radical pairs within the matrix.

THERE has been much interest in phosphorylcarbenes,[2] which have become conveniently available from the photolysis or thermolysis of phosphoryldiazo-compounds,
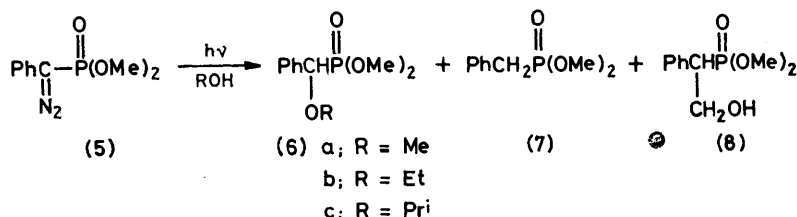
because they can be used to introduce the phosphoryl group into organic compounds, as in the phosphorylcyclopropanation of alkenes or arenes and in the phosphorylcyclopropenation of alkynes. When phenylphosphorylcarbenes are generated photolytically from diazo-compounds in the presence of alcohol, they react mainly in two ways [2] depending on the substituent R on phosphorus: by one route the phosphine oxides (2) are formed with direct O–H insertion of the phosphorylcarbene, by the other the phosphinic acid derivatives (4) are formed by phosphorylcarbene→methylenephosphine oxide (3) rearrangement, followed by nucleophilic addition of alcohols. Phenylphosphorylcarbenes (1; R = OR′) react with methanol predominantly by the O–H insertion pathway to give the ether (2) in high

RESULTS AND DISCUSSION

Direct irradiation of dimethyl α-diazobenzylphosphonate in methanol was carried out with a Halos

(300 W) high-pressure mercury arc without filter. The reaction was complete within 1 h when nitrogen ceased to be evolved and the yellow solution became colourless. Silica-gel chromatography of the reaction mixture gave dimethyl α-methoxybenzylphosphonate (6a) in 70% yield along with a small amount of dimethyl benzylphosphonate (7) (<3%). The identity of (6a) was confirmed on the basis of spectral data. The n.m.r. spectrum of (6a) showed a sharp singlet (3 H) at δ 3.38, characteristic of a methoxy-group, and a doublet (1 H) at δ 4.53 with $^2J_{PH}$ 16.0 Hz due to a benzylic methine proton adjacent to phosphorus. The phosphorus methoxy-groups in (6a) appeared as two doublets, showing a doubling of resonance compared with the starting compound (5); this is because the methoxy-

yield along with a small amount of the double hydrogen-abstraction product. We found, however, that the reactions of phosphorylcarbenes photolytically generated in alcohols are strongly temperature dependent, double hydrogen-abstraction being favoured at low temperatures (−72 °C) in solution, and at much lower temperatures (−196 °C) in alcoholic matrices C–H insertion occurring at the expense of the O–H insertion.

groups in (6) are diastereotopic due to the molecular chirality imposed by the chiral centre on the benzilic carbon, whereas the methoxy-groups in (5) are enantiotopic.[3]
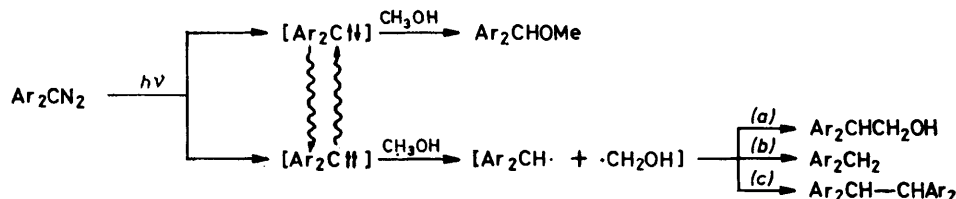
Compound (5) was next photolysed at −196 °C in a matrix of methanol, containing ca. 10% (v/v) of ethanol to obtain a uniform matrix. Irradiations were carried out in quartz tubes suspended in a transparent Dewar

flask in 30-min cycles, followed by thawing and homo-genizing in the dark and, subsequently, refreezing, which was continued until the yellow colour faded. The rate of the decomposition was very slow at this temperature and it took ca. 30—40 h to destroy all the diazo-com-pound. The reaction mixture was separated by silica-gel chromatography into two principal components. The first component (46 mg) eluted rapidly from the column and was easily identified as a 4 : 1 mixture of (6a) and (7) by spectral comparison with authentic specimens. The second, main component (162 mg, 70%) eluted slowly and was characterized as the alcohol (8), arising from the insertion of phosphorylcarbene into the C–H bonds of methanol, by n.m.r. and mass spectroscopy. The n.m.r. spectrum clearly lacked a C-methoxy singlet or a PhCH doublet; instead it showed a characteristic doublet ($^2J_{PH}$ 21.5 Hz) of triplets ($^3J_{HH}$ 7.0 Hz) at δ 3.28 and a multiplet at δ 4.10, in addition to a broad singlet at δ 1.2 which was exchangeable with D_2O. The mass-spectral fragmentation provided further evidence for the assigned structure. In addition to a parent ion at m/e 230 of low intensity (10%), the base peak appeared at m/e 220, corresponding to a McLafferty-type rearrange-ment, which has also been observed [4] as the main frag-mentation path in the mass spectrum of β-hydroxy-carboxylates.

When the photolysis was conducted in ethanol or propan-2-ol solution at room temperature, O–H insertion

(9) a; R_1 = Me, R_2 = H   (10) a; R = H   (11)
    b; R_1 = R_2 = Me   b; R = Me
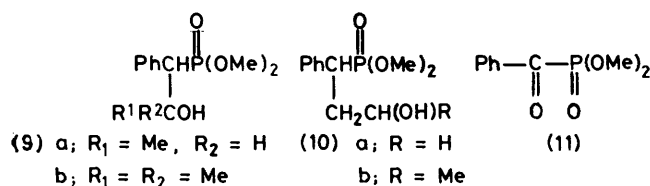
products were obtained again as the main products (16—25%), with only small amounts of the double hydrogen-abstraction product (7) (2—3%) and C–H

decrease rather drastically in ethanol and propan-2-ol runs, while the double hydrogen-abstraction product (7) concurrently becomes an important product as the

TABLE 1

Temperature dependence of product distributions in the photolysis [a] of (5) in alcohols

ROH	Temperature (°C)	Relative product yields (%) [b]				
		(6)	(7)	(8 or 9)	(10)	Total isolated yield (%)
MeOH	27	98.4	1.6	c		70
	3	95.2	4.8	c		
	−72	95.8	3.8	c		
	−196	17.8	5.6	76.5		92
EtOH	27	84.7	5.6	8.6	1.1	30
	3	76.9	10.1	11.7	1.3	
	−72	48.3	25.9	22.5	3.3	
	−196	11.4	14.0	67.7	6.9	94
Pr^{i}OH	27	60.8	12.1	19.2	7.9	26
	3	48.4	31.2	17.6	2.8	
	−72	7.3	72.2	18.1	2.4	
	−196	8.4	27.2	50.0	14.4	95

[a] Control experiments demonstrated that product distribu-tions were essentially independent of irradiation time. [b] Other product (<5%) was dimethyl benzoyl phosphonate. [c] Trace.

temperature is lowered in solution to −72 °C. Dramatic and significant increases in the C–H insertion product then appear in each system studied when the reaction phase is changed from liquid to solid.

It has been proposed [5,6] that the O–H insertion is the characteristic reaction of singlet arylcarbenes generated by the photolysis of the corresponding diazo-compounds in alcohols, and hence (6) is apparently derived from a singlet phosphorylcarbene initially formed in the direct photolysis of (5). Triplet arylcarbenes, on the other hand, are expected to abstract hydrogen from the C–H bonds of alcohols to give radical pairs, which in turn undergo three competing reactions: [5,6] (a) recombination to the C–H ' insertion ' product; (b) abstraction of the second hydrogen to give a double hydrogen-abstraction product; and (c) dimerization to a radical dimeric

SCHEME

insertion products (9) and (10) (3—7%). Photolysis in frozen alcohol matrices again resulted in increases (60—70%) in the yields of (9) and (10), predominantly (9), at the expense of the O–H insertion product. In order to get additional insight into the temperature dependence of the phosphorylcarbene processes in alcohols, a series of irradiations was conducted on (5) as a function of temperature in more detail and monitored by g.l.c., as summarized in Table 1. From Table 1 it can be seen that the significant alterations in product distribu-tions appear as the temperature is lowered: the ethers

product, as depicted in the Scheme. It was possible [7] to generate the triplet phosphorylcarbene in solution by selectively exciting Michler's ketone in the presence of (5) by using a Corning CS-052 filter (>350 nm) so as to ensure absorption of 99% of the incident light by the photosensitizer. The results are shown in Table 2 along with the results in the direct runs for comparison. As is evident from Table 2, product distribution is markedly different from that found in direct photolysis. The dramatic increase in the yield of dimethyl benzoyl-phosphonate, a characteristic product from the reaction

of triplet carbene with oxygen, in non-degassed runs, obviously indicates that the photosensitization increases

TABLE 2

Photolysis of (5) sensitized with Michler's ketone in alcohols at 27 °C

ROH	Relative product yields (%)				
	(6)	(7)	(9)	(10)	(11)
EtOH [a]	48.3	11.1	5.6	1.7	33.3
b	63.4	26.4	8.4	1.8	d
c	83.4	5.5	8.5	1.0	1.5
Pr^{i}OH [a]	25.7	22.8	1.9	d	49.5
b	36.6	30.4	27.7	5.2	t[d]
c	58.4	11.6	18.4	7.6	4.0

[a] Not degassed. [b] Degassed at $<10^{-4}$ mmHg. [c] Direct photolysis in non-degassed solution. [d] Trace.

the proportion of triplet species. As expected, a substantial increase in the yields of the double hydrogen-abstraction product and the C–H insertion products was observed in degassed runs, with considerable suppression of ether formation. Other higher-boiling products not investigated may have included the radical dimer, since this type of compound has been obtained [8] in the photolysis of (5) in hydrogen-donor media, e.g. cyclohexene. Thus, it is concluded that both (7) and (9) + (10) (and probably the radical dimer) are derived from triplet phosphorylcarbene, as has been observed previously for other simper arylcarbenes.

It has been reported [9] that aryl- and benzoyl-diazomethanes, when photolysed in hydrocarbon matrices at −196 °C gave almost exclusively triplet carbenes which were detected spectroscopically and showed the chemical behaviour expected from triplet carbene upon thawing, e.g. hydrogen-abstraction and reaction with oxygen. More recently, Moss et al.[10,11] have shown that the stereospecific cyclopropanation observed in photolysis of phenyldiazomethane in olefin solution became less important in the photolysis in frozen-olefin matrices. Instead, large amounts of olefins were formed, which were shown to arise by abstraction–recombination reactions of the triplet carbene. When (5) was irradiated in frozen ethanol which had been saturated previously with oxygen, the emission of blue-white light was observed during warming-up of the sample in the dark, with the formation of benzoyl phosphonate (from the g.l.c. analysis). The emission of light is believed to be due to the reaction of triplet carbene with oxygen, and has been used [12] to detect the presence of the triplet carbene in the low-temperature photolysis of diazo-compounds. Further, the emission spectra of (5) in frozen ethanol at −196 °C consisted of a broad band ($\lambda_{max.}$ 462 and 497 nm) with a shoulder at longer wavelength (Figure). In accordance with the previous observation [9] with diphenylmethylene, when the matrix was allowed to thaw, the emission at 462 and 497 nm disappeared, with concomitant appearance of a new emission spectrum, which was identified as the phosphorescence of benzoyl phosphonate (11) (see Figure). These results strongly suggest that the key intermediate leading to the C–H insertion products in the solid-phase experiments is also triplet phosphoryl-

carbene. Thus, we suggest here the abstraction–recombination mechanism rather than the direct insertion to rationalise the formation of the C–H ' insertion ' products in the matrix experiments. The observed difference in the chemical behaviour of triplet carbenes generated in the liquid and solid phases reflects, at least in part, on the mobility of members of radical pairs. It is possible that the triplet carbenes abstract hydrogen from the C–H bonds of alcohols to form radical pairs which recombine with high efficiency to give coupled products, i.e. the C–H ' insertion ' product in the matrix environment, whereas in the liquid phase the member of the pairs would diffuse apart to yield (7).
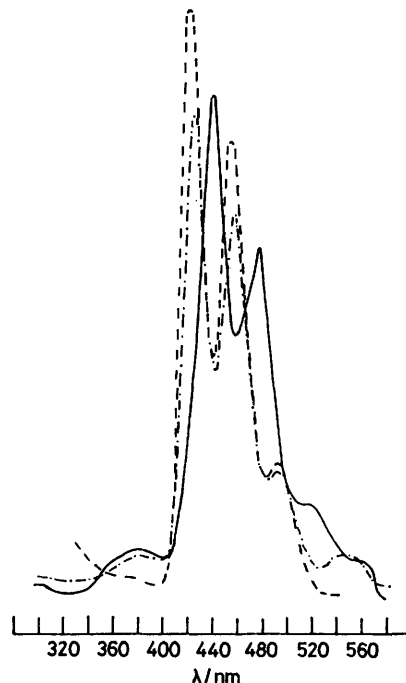
Emission spectra in ethanol at −196 °C; (——), (5) ; (— · — · —), the irradiated sample after warming to room temperature and re-cooling to −196 °C; (— — —), (11)

The reason for the marked reduction of the ether yield at lower temperature is then an important question. Moss et al.[10] have offered two explanations for the matrix effect to favour triplet chemistry, i.e., (i) a rapid decay of the initially formed singlet carbene to the triplet in a rigid matrix, and (ii) the effect on kinetics of the competitive intermolecular singlet and triplet carbene processes occurring within it. The first explanation seems unlikely in this case since the substantial yield of the ether even in the sensitized experiment (Table 2) apparently suggests that rapid and reversible triplet–singlet equilibrium is involved in the present system as in other arylcarbene reaction.[5,6] The second explanation may be more likely in this special system, since it has been proposed [5] that O–H insertion reactions of singlet carbenes involve ionic species, i.e. carbonium ions and/or ylides, which might be greatly stabilized by solvation. Such solvation might become less important in the solid phase and hence O–H insertion becomes less important

compared to other radical process of triplet carbene. Alternatively, a possibility which might be related to the marked reduction in ether formation at lower temperatures is the temperature-dependence of the acidity of alcohols. As is evident from Table 1, the reactivity of alcohols toward carbenes increases with increasing acidity of the hydroxy group. Careful study [13] of the effect of temperature on the electronic spectra of aceanthrenone derivatives in alcohol indicated the absence of hydrogen-bonding at very low temperature. These observations might suggest that the acidity of alcohols would decrease as the temperature is lowered. At lower temperatures, consequently, such effects are sufficient to raise the activation energy of the O–H insertion reaction to an extent which permits predominant formation of the C–H ' insertion ' products.

Complete absence of the product derived from methylenephosphine oxide even in solid runs at −196 °C is in apparent contrast with the result [11,14] for the matrix photolysis of 1-phenyldiazoethane, in which singlet carbene, restricted in the matrix, gives mainly the intramolecular rearrangement product, styrene, and intermolecular reactions from both singlet and triplet carbenes are suppressed. An explanation of the difference must include the relative migratory aptitude between the H and OR groups established [15] in solution-phase experiments. It is very tempting to suppose that there may be much greater hindrance to the motion of an OR group compared to H in a rigid environment.

Finally, a similar temperature dependence of the product distributions is observed with other α-diazobenzylphosphonates, $PhCN_2P(O)(OR)_2$ [(12) a; R = Et; b, R = Pr^i; c, R = Bu^i]. Interestingly, g.l.c.–mass spectral analysis of the reaction mixture demonstrated that no trace of products derived from an intramolecular C–H insertion reaction were formed even in the irradiations of di-isopropyl (12b) and di-isobutyl esters (12c) under any of the conditions employed, although molecular model shows that one of the alkyl groups can be in close proximity to the divalent carbene centre.

In conclusion, we find that the photolysis of (1) in frozen alcohols leads to triplet phosphorylcarbene which yields C–H insertion products in high yield; the method would be expected to be applicable to other carbenes as well, and hence provide a carbene route to the C–H insertion products which have been [16] only minor products in solution-phase experiments. It would also be expected [17] to be a means of marking the hydrophobic residues near the active site of enzymes if the reaction is applied to photolysis of diazo-acetylated enzymes.

EXPERIMENTAL

Infrared spectra were determined on a JASCO IR-G recording spectrometer. Hydrogen-1 nuclear magnetic resonance spectra were determined on a JEOL JNM-MH-100 n.m.r. spectrometer in $CDCl_3$ solution containing 5% $SiMe_4$: chemical shifts are in p.p.m. downfield from $SiMe_4$. G.l.c.–mass spectra were obtained on a Shimadzu GC-MS 1000 spectrometer using a column consisting of Silicone OV-17 on Shimalite (5.0 mm × 2.0 m). Ultraviolet and fluores-

cence spectra were measured with a Shimadzu UV 250 recording spectrometer and a Hitachi MPF-2A spectrofluorometer, respectively. G.l.c. analyses were performed on a Yanagimoto model G-800 using a 2.0 m × 5.0 mm column packed with 10% SE-30 on 60—80 mesh Diasolid L. Woelm silica gel (activity III) was always used for column chromatography.

Materials.—Benzoylphosphonates were prepared [18] by the Michaelis–Arbuzov reaction of benzoyl chloride with trialkyl phosphite. α-Diazobenzylphosphonates (5) and (12) were prepared [18] by the Bamford–Stevens reaction of the corresponding tosylhydrazones of benzoylphosphonates and purified by passage down a small column of neutral alumina. Benzylphosphonates were prepared [3] by the treatment of benzyl bromide with trialkyl phosphites. All solvents were purified by standard techniques.

Irradiations.—All irradiations were conducted using a Halos 300-W high-pressure mercury lamp with a water-cooled quartz jacket. For preparative-scale irradiation, a quartz tube containing 25 ml alcoholic solution of the diazo-compound (*ca.* 250 mg) was suspended in a transparent quartz Dewar flask filled with coolant, and irradiated without filter until the yellow solution became colourless. The coolants were water (27 °C), ice–water (3 °C), solid CO_2–ethanol (−72 °C), and liquid nitrogen (−196 °C). For solid-phase irradiations, the mixture was periodically warmed in the dark until the rigid glass or solid melted so that mixing could occur. For product identification, the irradiation mixtures were concentrated on a rotary evaporator below 25 °C, and individual components were isolated by column chromatography and characterized either as described below or by comparison with authentic specimens. The irradiations outlined in Table 1 were conducted in a degassed ($<10^{-4}$ mmHg) and sealed quartz tube of 5.0 ml capacity and the relative yields were determined by g.l.c. analysis. Sensitized photolyses were conducted in Pyrex tubes containing (5) and alcohols which were saturated with Michler's ketone, using filtered light with a Corning CS-052 filter. Control runs showed that no reaction occurred in the absence of light in the temperature range studied.

Irradiation of (5) *in Methanol at Room Temperature.*—In a typical run, a solution of (5) (252 mg) in methanol (25 ml) was irradiated at room temperature for 1 h. After removal of solvent under reduced pressure, the residue was chromatographed using chloroform as eluant to afford dimethyl α-methoxybenzylphosphonate (6a) as a colourless oil (177 mg); $v_{max.}(CHCl_3)$ 1 600, 1 490, 1 450, 1 245, and 1 030 cm⁻¹; δ 3.38 (3 H, s, OMe), 3.64 (3 H, d, ^3J 10.2 Hz, POMe), 3.71 (3 H, d, ^3J 10.2 Hz, POMe), 4.53 (1 H, d, ^2J 16.0 Hz, PhC*H*), and 7.15—7.60 (5 H, complex, Ph); *m/e* 230 (M^+) 200, 122, 121, 105, 104, 91, and 77.

Irradiation of (5) *in Frozen Methanol at* −196 °C.—A mixture of (5) (250 mg), ethanol (2.5 ml), and methanol (22.5 ml) was placed in a quartz tube fitted with a serum cap to which a balloon was connected through a syringe for pressure release. The tube was immersed directly in a transparent quartz Dewar flask containing liquid nitrogen and irradiated, with occasional rotation. Photolyses were carried out in cycles of 30-min irradiation, followed by thawing in the dark, and refreezing. Column chromatography afforded first a colourless oil (46 mg), which was identified as an unresolved mixture (4 : 1) of (6a) and dimethylbenzylphosphonate (7) by g.l.c. and n.m.r. The second fraction (162 mg, 70%) was identified as the alcohol (8); $v_{max.}(CHCl_3)$ 3 350, 1 600, 1 490, 1 450, 1 230, and 1 040 cm⁻¹; δ 1.27

(1 H, s, OH), 3.28 (1 H, d of t, ^2J 21.5 Hz, ^3J 7.0 Hz, PhCH), 3.47 (3 H, d, J 10.5 Hz, POMe), 3.65 (3 H, d, ^3J 10.5 Hz, POMe), 4.17 (2 H, m, CH_2OH), and 7.32 (5 H, s, Ph); m/e 230 (M^+), 200, 168, 153, 118, 105, 104, 92, 91, and 78.

Irradiations of (5) *in Ethanol.*—Using ethanol as solvent in the above procedure at room temperature gave dimethyl α-ethoxybenzylphosphonate (6b) (25%); $\nu_{max.}$(CHCl$_3$) 1 600, 1 490, 1 450, 1 245, and 1 040 cm^{-1}; δ 1.24 (3 H, t, ^3J 7.1 Hz, CH$_2$CH_3) 3.64 (2 H, q, ^3J 7.1 Hz, OCH_2CH$_3$), 3.58 (3 H, d, ^3J 10.2 Hz, POMe), 3.72 (3 H, d, ^3J 10.2 Hz, POMe), 4.66 (1 H, d, ^2J 16.0 Hz, PhCH), and 7.14—7.60 (5 H, complex, Ph); m/e 244 (M^+), 228, 200, 135, 134, 118, 107, 79, and 77.

Irradiation of (5) in frozen ethanol at −196 °C afforded the alcohols (9a) and (10a) (63.6 and 6.5% respectively). (9a); $\nu_{max.}$(CHCl$_3$) 3 050, 1 600, 1 490, 1 450, 1 230, and 1 043 cm^{-1}; δ 1.28 (1 H, s, OH), 1.14 (3 H, d, ^3J 6.7 Hz, CHCH$_3$), 3.04 (1 H, d of d, ^2J 23.2 Hz, ^3J 7.0 Hz, PhCH), 3.41 (3 H, d, ^3J 10.6 Hz, POMe), 3.75 (3 H, d, ^3J 10.6 Hz, POMe), 4.50 (1 H, m, CHOH), and 7.10—7.55 (5 H, complex, Ph); m/e 244 (M^+), 200, 168, 118, 105, 104, 92, 91, and 79. (9b); $\nu_{max.}$(CHCl$_3$) 3 350, 1 600, 1 490, 1 450, 1 232, and 1 045 cm^{-1}; δ 1.25 (1 H, s, OH), 2.23 (2 H, m, CH$_2$), 2.82—3.82 (3 H, complex), 3.52 (3 H, d, ^3J 10.5 Hz, POMe), 3.70 (3 H, d, ^3J 10.5 Hz, POMe), and 7.20—7.50 (5 H, complex, Ph); m/e 244 (M^+), 212, 200, 168, 117, and 118.

Irradiations of (5) *in Propan-2-ol.*—Using propan-2-ol as solvent in the above procedure at room temperature gave dimethyl α-2-propoxybenzylphosphonate (6c) (17%); $\nu_{max.}$(CHCl$_3$) 1 600, 1 492, 1 230, and 1 030 cm^{-1}; δ 1.19 (6 H, d, ^3J 7.2 Hz, CHMe_2), 3.65 (3 H, d, ^3J 10.2 Hz, POMe), 3.73 (3 H, d, ^3J 10.2 Hz, POMe), 3.5—3.9 (1 H, m, CHMe$_2$), 4.81 (1 H, d, ^2J 16.0 Hz, PhCH), and 7.15—7.60 (5 H, complex, Ph); m/e 258 (M^+), 200, 199, 150, 149, 108, 107, and 105.

Irradiation of (5) in frozen propan-2-ol at −196 °C afforded the alcohols (9b) and (10b) (47.5 and 13.7% respectively). (9b); $\nu_{max.}$(CHCl$_3$) 3 350, 1 600, 1 450, 1 235, and 1 030 cm^{-1}; δ 1.31 (6 H, d, J 7.2 Hz, CMe_2), 3.18 (1 H, d,

^2J 12.2 Hz, PhCH), 3.37 (3 H, d, ^3J 10.1 Hz, POMe), 3.66 (3 H, d, ^3J 10.1 Hz, POMe), and 7.05—7.50 (5 H, complex, Ph); m/e 258 (M^+), 200, 168, 131, 118, 117, 105, 104, 92, and 91. (10b); $\nu_{max.}$(CHCl$_3$) 3 350, 1 600, 1 450, 1 235, and 1 030 cm^{-1}; δ 1.15 (3 H, d, ^3J 6.5 Hz, CHCH_3), 2.08 (2 H, m, CH_2), 3.20—3.95 (2 H, complex), 3.47 (3 H, d, ^3J 10.2 Hz, POMe), 3.65 (3 H, d, ^3J 10.2 Hz, POMe), and 7.10—7.50 (5 H, complex, Ph); m/e 258 (M^+), 226, 214, 200, 168, 131, 130, 118, 117, and 105.

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