Photolysis of α-Diazobenzylphosphonates in Alcoholic Matrices at 77 K

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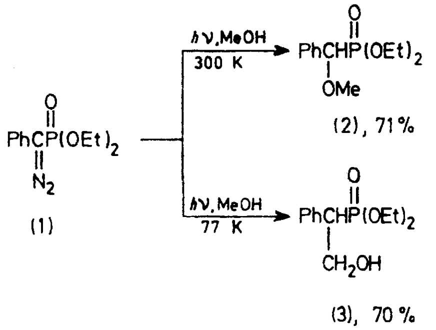
Summary Direct photolysis of α-diazobenzylphosphonates in alcohols at 300 K mainly gives the O–H insertion product, whereas in alcoholic matrices at 77 K it results in the C–H insertion product in high yield at the expense of the O–H insertion product.

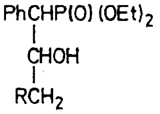
It is generally accepted that singlet carbene generated by direct photolysis of diazo-compounds in alcohols inserts into the O–H bond rather than the C–H bonds of the alcohol, while the main reaction pathway of carbenes generated by sensitized photolyses of diazo-compounds is double hydrogen abstraction.[1] Insertion into the C–H bonds of alcohols has been detected[2] but only as a minor pathway in the direct photolysis of some diazoacetates in these polar solvents. If such a reaction should occur in the photolysis of diazo-acetylated enzymes, it would provide[3] a unique means of marking the hydrophobic residues near the active sites of enzymes.



We report here that phosphonylcarbene, generated by direct photolysis of an α-diazophosphonate in frozen alcoholic matrices at 77 K, inserts into the C–H bonds of alcohols. Irradiation of a solution of (**1**) in degassed methanol in a quartz tube at 300 K for 5 h gave the α-methoxybenzylphosphonate (**2**, 71%) and traces of the benzylphosphonate (**3**, <0·5%). In contrast, irradiation of (**1**) in frozen methanol matrix at 77 K resulted in the C–H insertion product (**3**) in high yield (70%), and the yield of the O–H insertion product (**2**) was greatly reduced (16%). When the photolysis was conducted in ethanol or propan-2-ol solution at room temperature, O–H insertion products were obtained again as the main products (16—25%), with only small amounts of double hydrogen abstraction product (**4**) (2—3%) and C-H insertion products (**5**) and (**6**) (3—7%). Photolysis in frozen alcoholic matrices again resulted in an increase (60—70%) in the yields of (**5**) and (**6**) even in propan-2-ol which is a good hydrogen donor. The ratios of (**5** + **6**)/(**4**) found in the photolyses in ethanol and propan-2-ol matrices were 5·3 and 2·0, respectively.

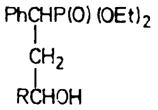
$\mathrm{PhCH_2P(O)(OEt)_2}$

(4)



$$\begin{array}{l}\mathrm{PhCHP(O)(OEt)_2}\\ \quad\mid\\ \mathrm{CHOH}\\ \quad\mid\\ \mathrm{RCH_2}\end{array}$$

(5) a, R = H
b, R = Me



$$\begin{array}{l}\mathrm{PhCHP(O)(OEt)_2}\\ \quad\mid\\ \mathrm{CH_2}\\ \quad\mid\\ \mathrm{RCHOH}\end{array}$$

(6) a, R = H
b, R = Me

When (**1**) was irradiated in ethanol glass which was saturated previously with oxygen, emission of blue-white light was observed during warm-up of the sample in the dark with the formation of benzoylphosphonate. The emission of light is believed[4] to be due to the reaction of triplet carbene with oxygen and has been used to detect the presence of the triplet carbene in the low temperature photolyses of diazo-compounds. These results strongly suggest that the key intermediate leading to the C–H insertion product in the solid phase experiments is triplet phosphonylcarbene.

It was possible,[5] on the other hand, to generate the triplet carbene in solution by selectively exciting Michler's ketone in the presence of diazo-compounds by using a Corning CS-052 filter (>350 nm) so as to ensure absorption of 99% of the light by the photosensitizer. Surprisingly, the triplet phosphonylcarbene generated under these conditions was relatively unreactive towards C–H insertion as is evident from the ratios of (**5** + **6**)/(**4**) found in ethanol and propan-2-ol (0·4 and 1·1, respectively).

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 carbene formed in the solid phase abstracts hydrogen from alcohol to give radical-pairs which would recombine to give coupled product in the matrix environment, whereas in the liquid phase the members of the pairs would diffuse apart to yield (**4**).

We conclude that the photolysis of (**1**) in frozen alcohols leads to triplet phosphonylcarbene which yields C–H insertion product in high yield and the reaction could be applicable to other carbenes.

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