

## An $\alpha$ -Diazophosphonic Acid Monoester: Synthesis, Stability, and Unexpected Photochemical Behaviour

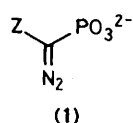
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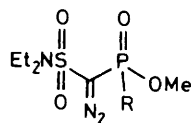
The  $\alpha$ -diazophosphonic acid monoester salt  $\text{Et}_2\text{NSO}_2\text{C}(=\text{N}_2)\text{P}(\text{OMe})\text{O}_2^-\text{Na}^+$  was synthesised and shown to undergo rearrangement to  $\text{Et}_2\text{NSO}_2\text{CH}_2\text{OPO}_3\text{Me}_2$  on photolysis in methanol ( $\lambda > 300 \text{ nm}$ ).

In connection with a study of  $\alpha$ -diazophosphonic acid di-anions (**1**) as potential photoaffinity labelling analogues of phosphate derivatives,<sup>1,2</sup> we prepared the monoester monanion (**2**) and investigated its stability and photochemistry. The novelty and unexpected nature of our photochemical findings prompt this communication.

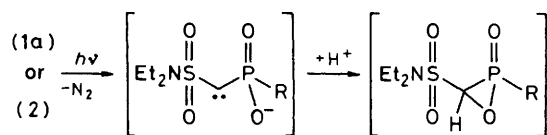
Treatment of the  $\alpha$ -diazo-ester (**3**) with methanolic sodium hydroxide (21 °C; 20 min) rapidly led to destruction of the diazo-functionality, as shown by the i.r. spectrum of the crude, red product obtained on evaporation. The monoanion (**2**) was prepared cleanly by monodealkylation of (**3**) in refluxing *t*-butylamine (18 h),<sup>3</sup> evaporation, ion exchange (Dowex



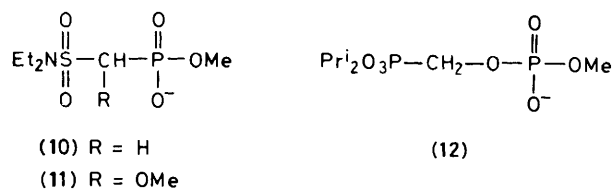
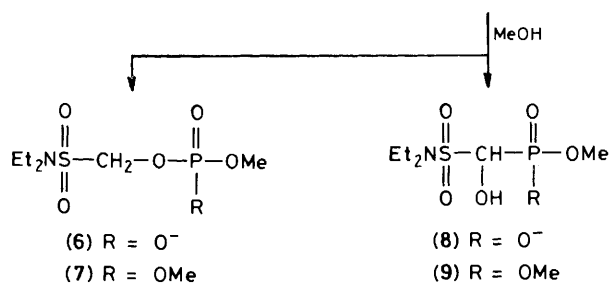
- a; Z = Et<sub>2</sub>NSO<sub>2</sub>  
 b; Z = Pr<sup>i</sup><sub>2</sub>O<sub>3</sub>P  
 c; Z = Me<sub>2</sub>NCO



- (2) R = O<sup>-</sup>  
 (3) R = OMe



- (4) R = O<sup>-</sup>  
 (5) R = OMe



50W-X8; Na<sup>+</sup>-form), and lyophilisation. The sodium salt of (2) was fully characterised spectrally; most diagnostic of the diazo-functionality were the i.r. (film)  $\nu$  2090 cm<sup>-1</sup>, <sup>13</sup>C n.m.r.  $\delta$  61.5 p.p.m. (d,  $J_{CP}$  155 Hz), and u.v. spectra (0.2M-phosphate buffer; pH 9.0)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 232 (3.81) and 385 nm (1.59).

As expected, the monoanion (2) proved to be stable for extended periods in aqueous solution; no change in the u.v. spectrum was observed at pH 6.0 or 7.5 and 21 °C during 7 days. Loss of nitrogen from a C-protonated diazonium intermediate is hindered both sterically and electronically. Moreover, with the monoanion there is little driving force for dephosphorylation, which is the mode of decomposition of the dianions (1).<sup>1,2</sup>

The photochemistry of (2) was studied for a  $3.6 \times 10^{-3}$  M methanolic solution at 22 °C using a medium-pressure mercury immersion lamp equipped with a Pyrex filter ( $\lambda > 300$  nm). After evaporation of the solvent under reduced pressure, the residue was shown to consist of a single major component by <sup>1</sup>H n.m.r. spectroscopy. This material proved to be a neutral compound, and could be isolated from the organic

layer in 20–30% yield on partitioning the crude product between chloroform and water. The n.m.r. spectra (CDCl<sub>3</sub>) showed unambiguously that the compound was the phosphate (7): <sup>1</sup>H  $\delta$  1.23 (6H, t,  $J$  7.1 Hz), 3.37 (4H, q,  $J$  7.1 Hz), 3.85 (6H, d,  $J_{PH}$  11.3 Hz), and 4.82 (2H, d,  $J_{PH}$  8.5 Hz); <sup>13</sup>C  $\delta$  14.5, 42.1, 55.0 (d,  $J_{CP}$  6.4 Hz), and 75.7 p.p.m. (d,  $J_{CP}$  6.5 Hz); <sup>31</sup>P  $\delta$  0.84 p.p.m.† Particularly revealing is the low phosphorus-carbon coupling constant for the central CH<sub>2</sub> group, indicating that it is no longer directly attached to phosphorus, and the <sup>31</sup>P chemical shift, characteristic of a trialkyl phosphate rather than a phosphonate.§

Among the minor photoproducts we saw no evidence for the photoreduction or methanol insertion products (10) and (11), expected by analogy with the photochemical behaviour of the diester (3).<sup>2</sup> The crude photolysate of (2) was examined by h.p.l.c. (Waters Associates  $\mu$ Bondapak C18 analytical column, eluted with water), but no peaks corresponding to the monoanions (10) and (11) were present. (Authentic samples of these materials were prepared by *t*-butylamine-induced dealkylation of the diester precursors.<sup>2</sup>) Nor did we detect the  $\alpha$ -hydroxy-diester (9), expected by analogy with the major product observed on photolysis of the dianion (1a).<sup>2</sup> The  $\alpha$ -hydroxysulphonamide (9) is an unstable compound; however, we have observed it previously on photolysis of the diester (3) in water. The possibility that it was formed on photolysis of (2) in methanol and underwent subsequent base-catalysed decomposition cannot be ruled out.

What is the mechanism by which the oxygen insertion product (7) arises? To our knowledge, no such rearrangement of an  $\alpha$ -diazophosphonate has been reported,<sup>4</sup> although Chowdhry and Westheimer have observed a somewhat analogous process on photolysis of *p*-tolylsulphonyldiazoacetic esters.<sup>5</sup> We suggested previously<sup>2</sup> that an oxaphosphiran (4) was involved in the Wolff-like photochemical rearrangements of the  $\alpha$ -diazophosphonates (1a) and (1b). Formation of a similar intermediate (5), followed by phosphorus-carbon bond cleavage, would lead to the observed phosphate (7). This process is clearly related to the  $\alpha$ -hydroxyphosphonate-to-phosphate rearrangement.<sup>6</sup>

Of further interest is the discovery on re-examination of our results from photolysis of the dianions (1a) and (1b)<sup>2</sup> that the analogous oxygen-insertion products (6) and (12) are minor but significant products. The central methylene group of the sulphonamide (6) shows n.m.r. resonances at  $\delta$  (<sup>1</sup>H) 4.9 (2H, d,  $J_{PH}$  7 Hz) and  $\delta$  (<sup>13</sup>C) 75.3 p.p.m. (d,  $J_{CP}$  6.1 Hz); the resonance for the analogous methylene group of (12) appears as a doublet of doublets:  $\delta$  (<sup>1</sup>H) 4.2 (2H, dd,  $J$  9 and 5 Hz) and  $\delta$  (<sup>13</sup>C) 58.7 p.p.m. (dd,  $J$  172 and 6.1 Hz). Both modes of oxaphosphiran cleavage are therefore apparently possible in the anionic series.¶

† A molecular ion was not observed in electron-impact mass spectra, although an accurate mass determination of the fragment ions allowed positive identification of the four major peaks:  $m/z$  (% of base peak) 140 (55%, C<sub>3</sub>H<sub>8</sub>O<sub>4</sub>P), 139 (39%, C<sub>3</sub>H<sub>8</sub>O<sub>4</sub>P), 109 (100%, C<sub>2</sub>H<sub>6</sub>O<sub>3</sub>P), and 72 (69%, C<sub>4</sub>H<sub>10</sub>N). Using the fast atom-bombardment technique, the following major peaks were observed:  $m/z$  (% of base peak) 276 (5.4%,  $M + 1$ ), 169 (10%), 150 (3%), 139 (28%), 120 (54%), and 109 (100%). We thank Dr Ken Straub of the Space Sciences Laboratory, University of California, Berkeley, for the mass spectra.

§ Compare for example: Et<sub>2</sub>NSO<sub>2</sub>CHOHP(OMe)<sub>2</sub> (+19.67 p.p.m.), Et<sub>2</sub>NSO<sub>2</sub>CH(OMe)P(O)(OMe)O<sup>-</sup>Na<sup>+</sup> (+7.87 p.p.m.); positive  $\delta$  values, downfield from Me<sub>3</sub>PO<sub>4</sub> at  $\delta$  3.09 p.p.m. in CDCl<sub>3</sub>.

¶ Irradiation of (2) in ethanol produced the mixed triester (6; R = Et).

† All n.m.r. spectra were recorded in D<sub>2</sub>O unless otherwise indicated; <sup>1</sup>H spectra are referenced to external Me<sub>4</sub>Si and <sup>13</sup>C spectra to internal dioxan at 66.5 p.p.m. with respect to Me<sub>4</sub>Si.

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