Photochemical Carbon–Phosphorus Bond Cleavage of Nitro-substituted Benzylphosphonic Acids

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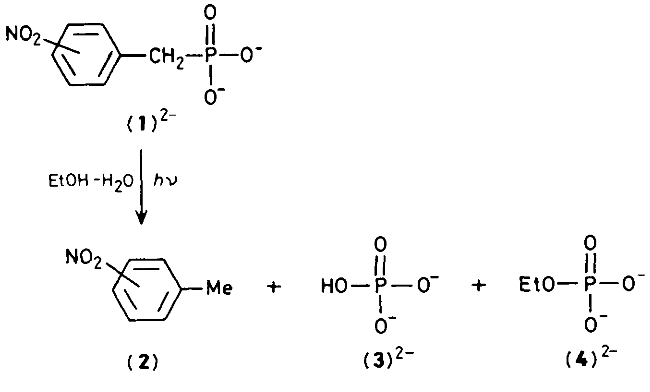
Upon u.v.-irradiation, the C–P bond of *p*-nitrobenzylphosphonate is more readily cleaved to give a monomeric metaphosphate anion as intermediate than those of *o*- and *m*-derivatives.

A monomeric metaphosphate anion has been postulated as an intermediate in the hydrolysis of phosphate esters and has been suggested as an essential phosphorylating agent in the reactions involved in intermediary metabolism.[1] Recently, the anion generated by decomposition of a β-halogenoalkylphosphonate anion was used as a new phosphorylating reagent.[2]

Upon u.v.-irradiation of *p*-nitrobenzylphosphonic acid (**1a**)† in a basic 50% ethanol solution (v/v) using a high-pressure mercury lamp with a Pyrex filter, the C–P bond was cleaved with a high efficiency to give *p*-nitrotoluene (**2a**), and dianions of orthophosphoric acid (**3**) and ethyl dihydrogen phosphate (**4**) [mole ratio $(3)^{2-}:(4)^{2-} = 2.9$]. The quantum yield of the C–P bond cleavage was 0.76. The dianions of *m*- and *o*-nitrobenzylphosphonic acids† [$(\mathbf{1b})^{2-}$ and $(\mathbf{1c})^{2-}$] also undergo C–P bond cleavage although their photochemical reactivities were much lower than that of the *p*-derivative (**1a**) (Table 1).

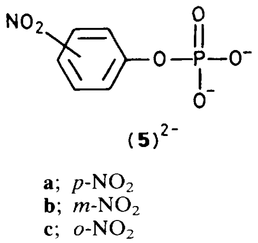
It is well known that upon u.v.-irradiation of the anions of nitrophenyl phosphates (**5**) in aqueous solution, the O–P bond is cleaved to give nitrophenol and the anion (**3**). The *m*-nitro-derivative (**5b**) undergoes a remarkably more rapid hydrolysis than the *p*- (**5a**) and *o*-nitro-derivatives (**5c**).[3—7] This *meta* transmission effect contrasts with the long established *ortho–para* transmission of ground state chemistry. This observed photochemical reactivity has been shown to agree with expectation based on the first electronic excited state LCAO MO electron distributed by Zimmerman.[5]

The *para*-transmission effect of the nitro group in (**1**) contrasts with the *meta*-transmission in (**5**). The difference in behaviour between (**1**) and (**5**) results from the difference in the mechanism. The other characteristic features of the behaviour of (**1**) are summarized as follows. (i) Absorption maximum of (**1**) (290 nm in H_2O, pH <6) shifts to longer wavelength on increasing the pH of the solution (305 nm, pH >9). This shift may be due to an intramolecular charge transfer. (ii) The quantum yield of C–P bond cleavage of (**1a**) is significantly higher than that of photolysis of (**5b**) (Table 1). (iii) The photolysis of (**5b**) occurred above pH 3, at the state of



$(1)^{2-}$

(2) $(3)^{2-}$ $(4)^{2-}$



$(5)^{2-}$

a; *p*-NO_2
b; *m*-NO_2
c; *o*-NO_2

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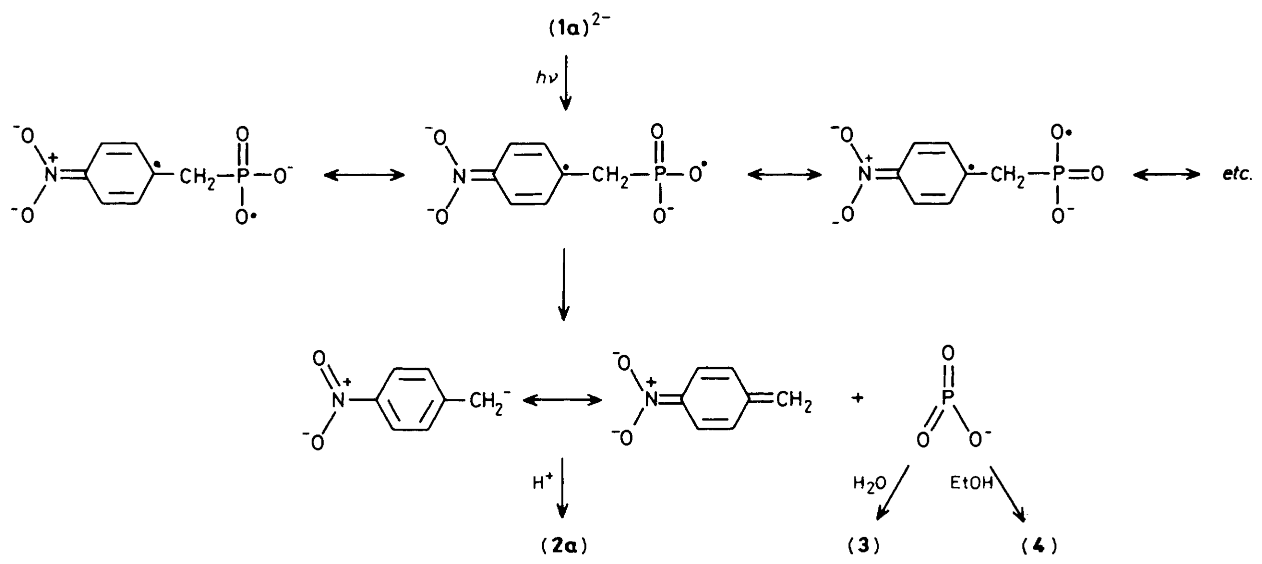
† The phosphonic acids (**1**) were obtained by hydrolysis of the corresponding diethyl nitrobenzylphosphonates, which were prepared by Arbuzov reaction of the corresponding nitrobenzyl bromides and triethyl phosphite, respectively. (**1a**); m.p. 228—229 °C, u.v. (50% EtOH, pH 12) $\lambda_{max.}$ 305 nm (ε 10500), δ_H [D_2O, NaOD, sodium 3-trimethylsilylpropanesulphonate (DSS)] 2.98 (2H, d, CH_2, J_{HP} 20 Hz), 7.2—8.2 (4H, m). (**1b**); m.p. 186—187 °C, u.v. (50% EtOH, pH 12) $\lambda_{max.}$ 280 nm (ε 7300), δ_H (D_2O, NaOD, DSS) 2.84 (2H, d, CH_2, J_{HP} 18.0 Hz), 7.1—8.0 (4H, arom, m). (**1c**); m.p. 190—191 °C, u.v. (50% EtOH, pH 12) $\lambda_{max.}$ 270 nm (ε 6600), δ_H (D_2O, NaOD, DSS) 3.13 (2H, d, CH_2, J_{HP} 21.0 Hz), 7.1—8.0 (4H, arom, m).



Scheme 1

Table 1. Quantum yields of C–P bond cleavage of (1) and (5).[a]

	Quantum yield		Quantum yield
(1a)	0.76[b]	**(5a)**	0.002[c]
(1b)	0.039[b]	**(5b)**	0.05[c]
(1c)	0.024[b]	**(5c)**	0.003[c]

[a] The quantum yields were determined on the basis of the yield of (**2**) generated and chemical actinometry using hexan-2-one (ref. 8). The quantum yield of acetone formation was taken as 0.25 in 2,2,4-trimethylpentane at room temperature. A 2 ml 2,2,4-trimethylpentane solution of hexan-2-one with an absorbance identical with that of the solution of (**1**) was irradiated for 1 h in a merry-go-round apparatus employing 313 nm monochromatic light using a high-pressure mercury lamp and a filter solution of 0.1% K_2CrO_4–0.1% K_2CO_3. The yields of (**2**) and acetone were determined by g.l.c. analysis. The photolyses were carried out with no more than 10% decomposition. [b] pH 12, 50% EtOH–H_2O. [c] 10 mmol dm^{-3} NaOH (ref. 7).

the monoanion, while C–P bond cleavage of (**1a**) occurred above pH 7, at the state of the dianion.[9] Ethyl *p*-nitrobenzylphosphonate $[ArCH_2P(O)(OEt)O^-]$[‡] did not undergo C–P bond cleavage. (iv) Dianions of (**1a**), in the dark, do not react at all within 48 h at 40 °C. (v) This photochemical C–P bond cleavage was not essentially affected by the presence of oxygen, although the yield of (**2a**) was slightly reduced owing to formation of *p*-nitrobenzaldehyde. (vi) With a spectro multi-channel photo-detector (MCPD-110, Union Giken), a transient absorption band of *p*-nitrobenzyl anion (360 nm, $\tau_{1/2}$ 60 s) was observed after short time u.v.-irradiation of an aqueous solution of (**1a**) (10^{-5} mmol dm^{-3}, pH 12), which is similar to that reported by Margerum and coworker under similar conditions.[10] (vii) By XeCl excimer laser flash photolysis (15 ns flash of 308 nm light) a short-lived transient species having absorption maxima at about 300 and 500—800 nm was observed. This species decayed along with the formation of a *p*-nitrobenzyl carbanion. Both the decay and the formation rates followed first-order kinetics, and their rate constants were nearly of the same order ($0.7 \times 10^7\ s^{-1}$ and $1.2 \times 10^7\ s^{-1}$, respectively).

This photochemical C–P bond cleavage proceeds *via* a radical-anion by intramolecular electron transfer from the $-P(O)O_2^{2-}$ group to nitroaromatics; on this basis a simple rationale is provided to explain our observations (Scheme 1).

The dianions $(\mathbf{1b})^{2-}$ and $(\mathbf{1c})^{2-}$ give (**2b**) and (**2c**) at a quantum yield of only one-twentieth that of (**2a**) from $(\mathbf{1a})^{2-}$. The pronounced lower reactivity of the *m*-nitrobenzylphosphonate anion was different from the results reported by Margerum on the photolysis of nitrophenylacetate ions.[10]

Received, 6th May 1986; Com. 599

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[‡] Ethyl *p*-nitrobenzylphosphonate was prepared by nitration of ethyl benzylphosphonate with fuming nitric acid at 0 °C, m.p. 156—157 °C, u.v. (50% EtOH, pH 12) $\lambda_{max.}$ 290 nm (ε 10600), δ_H (D_2O, NaOD, DSS) 1.17 (3H, t, Me, J_{HH} 7.0 Hz), 3.10 (2H, d, PCH_2, J_{PH} 20 Hz), 3.80 (2H, quint, CH_2, J_{HH} 7.0, J_{PH} 7.0 Hz), 7.3—8.2 (4H, arom, m).