Photohydrolysis of 2,4,6-Trimethylpyrylium Perchlorate: Evidence for Isomerisation to an Oxoniabenzvalene Intermediate

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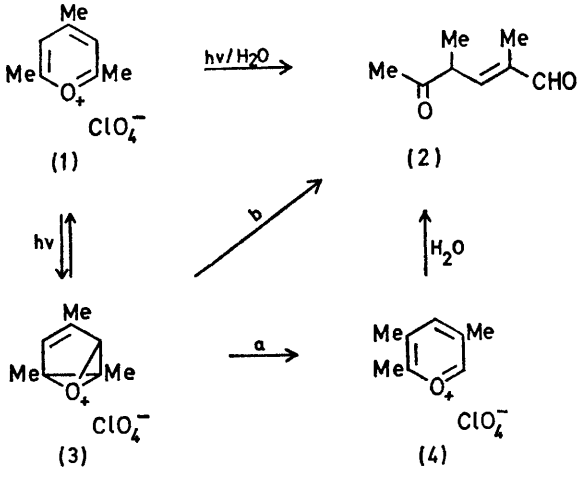
Summary U.v. irradiation of 2,4,6-trimethylpyrylium perchlorate (**1**) in water gives 2,4-dimethyl-5-oxohex-2-enal (**2**), possibly *via* an oxoniabenzvalene intermediate (**3**).

THE recently described[1] photohydrolysis of *N*-methylpyridinium chloride prompts us to report our study of an oxygen analogue, 2,4,6-trimethylpyrylium perchlorate (**1**). An aqueous solution of (**1**) (6×10^{-2} M), when irradiated (medium-pressure Hg arc, $\lambda > 270$ nm, under N_2, 25°), rapidly gave rise to polymeric material and a colourless oil (12%), *trans*-2,4-dimethyl-5-oxohex-2-enal (**2**), the i.r. and n.m.r. spectra being consistent with formulation (**2**).

Confirmation that the photoproduct had structure (**2**) came from its close resemblance to glutaconic dialdehyde: (i) yellow coloration with alkali, (ii) formation of a mono- and a bis-2,4-dinitrophenylhydrazone,† (iii) reaction with aqueous ethanolic ammonia to give 2,3,5-trimethylpyridine, identical in all respects with an authentic sample[2] (i.r., n.m.r., n_D; m.p. and mixed m.p. of picrates), and (iv) reaction with acetic anhydride in pyridine to give MeCO·CMe:CH·CMe:CH·OAc.†

Since the pyrylium salt (**1**) is stable in water in the absence of light, the simplest interpretation of the formation of (**2**) is that irradiation gives rise to the oxoniabenzvalene intermediate (**3**) analogous to the intermediates formed from the excited states of isoelectronic species such as benzene[3] and pyridinium salts.[1]‡ Re-aromatisation leads



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† Satisfactory elemental analyses and spectroscopic data were obtained for these compounds.

‡ A mechanism involving Dewar- and prismane-type intermediates is considered to be less likely on energy grounds.

to reversion to (**1**) or to the rearranged pyrylium salt (**4**), which, since it possesses a free α-position, might be expected to hydrolyse very rapidly to the *cis*-form of the keto-aldehyde (**2**) (Scheme). (*Cf.* the instability of the parent pyrylium cation.[4])

Upon irradiation of (**1**) in either anhydrous acetonitrile or trifluoroacetic acid, no (**4**) could be detected by n.m.r. spectroscopy. In terms of the above hypothesis, this implies that partition of the intermediate (**3**) between (**1**) and (**4**) favours the initial pyrylium salt (**1**) strongly. The keto-aldehyde (**2**), then, must be produced by rapid hydrolysis (and geometric isomerisation) of the small amount of (**4**) formed upon re-aromatisation of (**3**) (path a) with consequent displacement of the photoequilibrium. However, we cannot at present exclude an alternative possibility, namely, that (**2**) is formed from (**3**) by solvolytic processes not involving re-aromatisation (path b). The details of the processes and the photochemistry of other pyrylium salts are being investigated.

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[1] L. Kaplan, J. W. Pavlik, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1972, **94**, 3283.

[2] F. Bohlmann, A. Englisch, J. Politt, H. Sander, and W. Weise, *Chem. Ber.*, 1955, **88**, 1831.

[3] D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47.

[4] F. Klages and H. Träger, *Chem. Ber.*, 1953, **86**, 1327.