Light-induced 1,2-Transposition and 2,6-Bonding in 4-Ethyl-2,6-dimethylpyrylium Perchlorate

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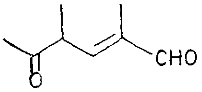
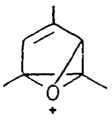
Summary U.v. irradiation of 4-ethyl-2,6-dimethylpyrylium perchlorate in water gives 2-ethyl-4-methyl-5-oxohex-2-enal (**8**) and *syn*- and *anti*-5-ethylidene-2,3-dimethylcyclopent-2-enone (**9**), all three products probably being formed *via* an oxoniabenzvalene intermediate (**6**).


(1)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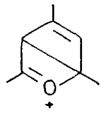
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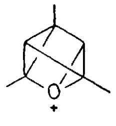
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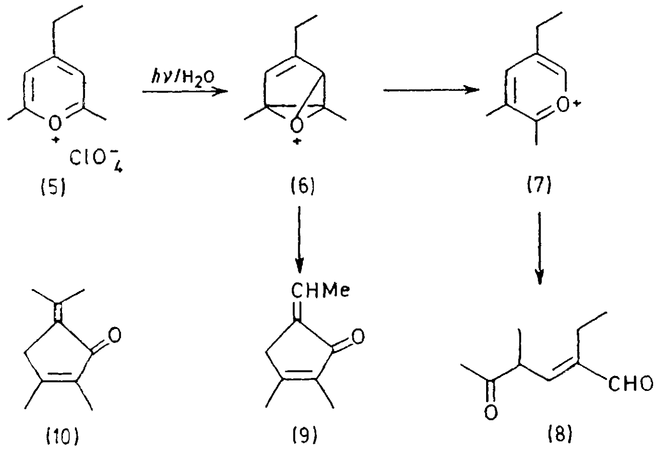
(5) (6) (7) (10) (9) (8)

RECENTLY, we described the photohydrolysis of 2,4,6-trimethylpyrylium perchlorate to give the unsaturated keto-aldehyde (**1**).[1] A 1,2-transposition mechanism involving the oxoniabenzvalene (**2**) was suggested, but the possibility of more drastic ring-scrambling *via* the 2,5-bridged Dewar ion (**3**) and the oxoniaprismane (**4**) could not be rigorously excluded.† We report here a study of 4-ethyl-2,6-dimethylpyrylium perchlorate (**5**), a compound in which the positional labelling is sufficient to discriminate between the two mechanisms.

Irradiation of an aqueous solution of (**5**) (7×10^{-2} M; medium-pressure Hg arc; $\lambda > 270$ nm; under N_2; 25°) gave as major product an oily ketoaldehyde (24%), which was shown by its spectra and those of the corresponding mono- and bis-2,4-dinitrophenylhydrazone to be 2-ethyl-4-methyl-5-oxohex-2-enal (**8**), the product expected from the oxoniabenzvalene mechanism *via* (**6**) and (**7**). A ring-scrambling mechanism analogous to the sequence trimethylpyrylium → (**3**) → (**4**) → (**1**) would have given not (**8**), but the isomeric keto-aldehyde 4-ethyl-2-methyl-5-oxohex-2-enal.

The valene mechanism was further supported by the isolation of compounds which were identified from their spectra as *syn*- and *anti*-5-ethylidene-2,3-dimethylcyclopent-2-enone (**9**; each 10%). These 2,6-bonded products are readily derivable in non-photochemical heterolytic steps from (**6**). Likewise, 4-isopropyl-2,6-dimethylpyrylium perchlorate gave compound (**10**) when irradiated under the same conditions.

Evidently, the photochemical analogies between pyridinium[2] and pyrylium salts are very close.[3]

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† On this mechanism, (**1**) arises *via* the Dewar structure formed by cleavage of a C–C and a C–O bond in the oxoniaprismane (**4**). *A priori*, one would have expected to obtain an additional product, *viz.*, 2,3-dimethyl-5-oxohex-2-enal, *via* cleavage of two C–C bonds in (**4**). It is not inconceivable, though, that there might be a strong preference for the former mode of cleavage of the prismane.

[1] J. A. Barltrop, K. Dawes, A. C. Day, and A. J. H. Summers, *J.C.S. Chem. Comm.*, 1972, 1240.

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

[3] *Cf.* also J. A. Barltrop, K. Dawes, A. C. Day, and A. J. H. Summers, *J. Amer. Chem. Soc.*, 1973, **95**, 2406.