Ring Permutations in the Photochemistry of Hydroxypyrylium Cations

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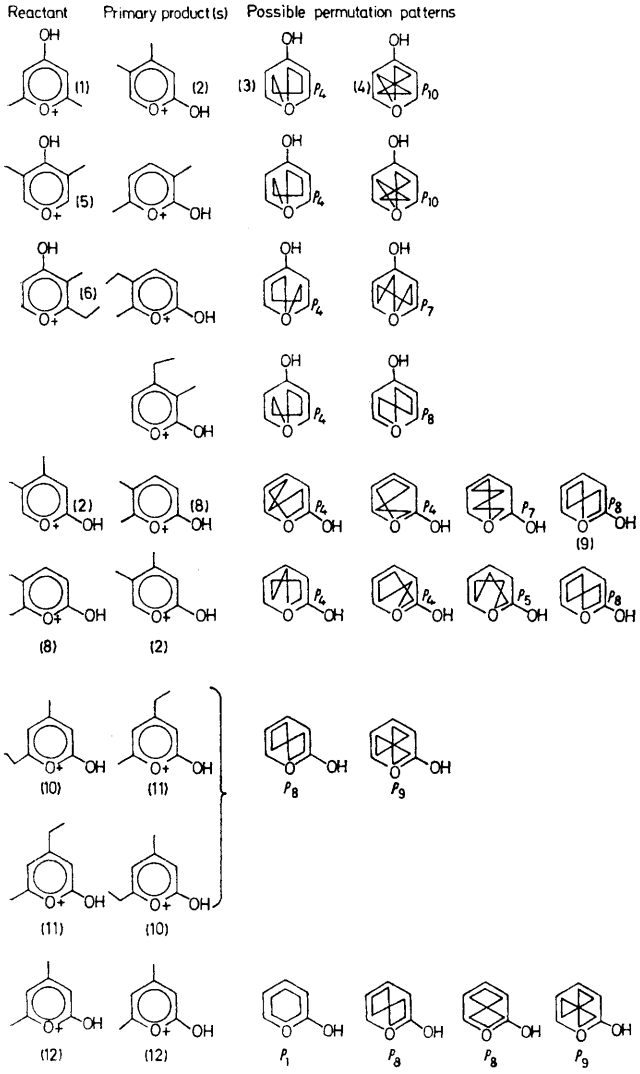
Summary Irradiation of various alkylated 2- and 4-hydroxypyrylium cations induces transpositions of the ring atoms, which when analysed by the formalism of permutation patterns define, for the first time, the fate of all the ring carbons in such processes.

WE have recently stressed the importance of tracing the fate of each ring atom in discussing aromatic phototransposition reactions, and have introduced the formalism of permutation patterns.[1] We report here the application of this approach to study the phototransposition reactions of 4-

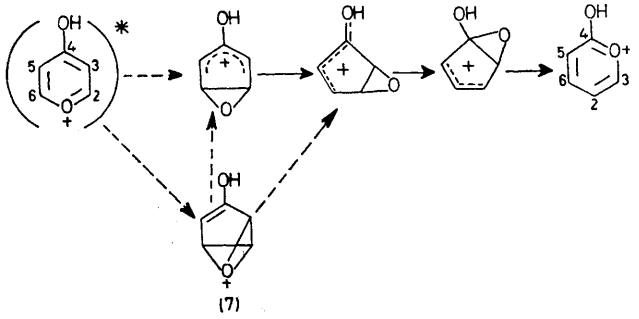
hydroxy- and 2-hydroxy-pyrylium cations, first reported by Pavlik and Clennan.[2]

TABLE. Primary products and permutation patterns in hydroxypyrylium phototranspositions.



Irradiation of the 4-hydroxypyrylium cation (**1**) in 98% sulphuric acid was reported[2] to give initially the 2-hydroxy isomer (**2**). This result is accommodated by two permutation patterns, P_4 (**3**) and P_{10} (**4**). (In these and similar diagrams, the lines within the hexagon show the atomic connections in the transposed product.[1]) To discriminate between these alternatives, we have irradiated† the 4-hydroxypyrylium cations (**5**) and (**6**), and obtained the primary products given in the Table. If we assume that varying the position and nature of alkyl substitution as in compounds (**1**), (**5**), and (**6**) introduces only minor perturbations that do not change the permutation pathway, then it is clear from the Table that the permutation pathway followed in these reactions is that formalised by the P_4 pattern oriented with respect to the hetero-atom, as shown in (**3**).

This characterisation of the permutation pattern very greatly restricts the range of conceivable mechanisms for the phototransposition of 4-hydroxy- to 2-hydroxy-pyrylium



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cations. Of various possible mechanisms consistent with the observed permutation pattern, we consider the most attractive to be those involving rearrangement of oxabicyclohexenyl cations (Scheme), which might be formed *via* an oxoniabenzvalene (**7**) or directly from the electronically excited reactant. *Ab initio* SCF calculations[3] support the view that 2,6-bonding is a highly probable consequence of electronic excitation of a 4-hydroxypyrylium cation.

Pavlik and Clennan found that further irradiation of the 2-hydroxypyrylium ion (**2**) gave the 5,6-dimethyl isomer (**8**).[2] Again we note that several permutation patterns account for the result (2 × P_4, P_7, P_8 in Table). We find that the conversion of (**2**) into (**8**) is reversible, which implies P_8, oriented as in (**9**), as the only common permutation pattern. [All P_4 patterns shown in the (**2**) and (**8**) entries in the Table are distinct by virtue of their different orientations in the ring.] Likewise, (**10**) and (**11**) are photointerconvertible, the possible patterns here being P_8 (**9**) or P_9. The permutation pattern common to all these substrates is P_8 (**9**). All these transpositions are clean and rapid reactions. In contrast, no phototransposition was observed with 3,6-dimethyl-2-hydroxypyrylium (**12**), even after prolonged irradiation. It seems inconceivable that the replacement of an ethyl group in (**10**) or (**11**) by a methyl group should have a profound effect upon the efficiency of transposition, and we must therefore assume that irradiation of (**12**) simply sends the molecule into itself by the common P_8 pattern (**9**). Pavlik and Clennan's mechanism,[2] involving skeletal 1,3-rearrangement of an intermediate Dewar structure, is consistent with the observed pattern of transposition, though alternative mechanisms also come to mind.

We are currently investigating the photochemistry of other alkylated hydroxypyrylium cations to test further our

† The pyrones, dissolved in conc. H_2SO_4 were irradiated with light (λ 254 nm) in a Rayonet reactor.

assumption here, that the mechanism of these reactions and therefore the permutation pathway is independent of alkyl substitution. Preliminary results upon the 2,5-dimethyl-4-hydroxypyrylium cation show that here too the major pathway is P_4 (**3**). A labelling study with the [2,6-^{14}C]-2,6-dimethyl-4-hydroxypyrylium cation also shows that the bonds linking the alkyl groups to the ring remain unbroken during transposition.

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[1] J. A. Barltrop and A. C. Day, *J.C.S. Chem. Comm.*, 1975, 177.
[2] J. W. Pavlik and E. L. Clennan, *J. Amer. Chem. Soc.*, 1973, **95**, 1697.
[3] J. A. Barltrop and S. C. R. Moore, to be published.