Phototranspositions of Alkyl-substituted Pyrylium Cations. Dependence upon Substitution Pattern

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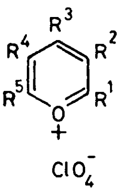
Summary U.v. irradiation of a series of tri-, tetra-, and penta-alkyl-substituted pyrylium perchlorates in acetonitrile resulted in phototransposition only when positions 3 and 5 were both alkyl-substituted; possible mechanisms involving 2,6-bonding are discussed in the light of the dependence upon the substitution pattern and a reinterpretation of the previously reported photohydrations of pyrylium cations is offered.

PHOTOTRANSPOSITIONS of 2- and 4-hydroxypyrylium cations[1] and 4-pyrones[2] are well established. However, the phototransposition of pyrylium cations bearing only alkyl-substituents has not hitherto been reported, though it was suggested as a possible stage in the photohydration of 2,4,6-trialkylpyrylium cations.[3] We describe here the first examples of a straightforward phototransposition in the alkylated pyrylium series and report a striking dependence upon the substitution pattern.

When irradiated in acetonitrile with 300 nm light at *ca.* 34 °C, 2,3,5,6-tetramethylpyrylium perchlorate **(1)**[4] was converted, through its lowest singlet excited state ($\pi\pi^*$), cleanly into the 2,3,4,6-tetramethyl isomer (**2**),† which was isolated by crystallisation, after complete destruction of the starting material, and shown to be identical with an authentic sample.[5]



(**3**): $R^1 = R^5 =$ Et; $R^2 = R^4 =$ Me; $R^3 =$ H
(**4**): $R^1 = R^2 =$ Et; $R^3 = R^5 =$ Me; $R^4 =$ H
(**5**): $R^1 =$ Et; $R^2 = R^4 = R^5 =$ Me; $R^3 =$ H
(**6**): $R^1 =$ Et; $R^2 = R^3 = R^5 =$ Me; $R^4 =$ H
(**7**): $R^1 = R^3 = R^5 =$ Me; $R^2 =$ Et; $R^4 =$ H
(**8**): $R^1 = R^2 = R^4 = R^5 =$ Me; $R^3 =$ Et
(**9**): $R^1 = R^3 = R^4 = R^5 =$ Me; $R^2 =$ Et
(**10**): $R^1 =$ Et; $R^2 = R^3 = R^4 = R^5 =$ Me

Similarly, 2,6-diethyl-3,5-dimethylpyrylium perchlorate (**3**) gave 2,3-diethyl-4,6-dimethylpyrylium perchlorate (**4**) upon irradiation, and 2-ethyl-3,5,6-trimethylpyrylium perchlorate (**5**) gave a mixture of the 2-ethyl-3,4,6-trimethyl (**6**) and the 3-ethyl-2,4,6-trimethyl (**7**) isomers, both being primary products. 4-Ethyl-2,3,5,6-tetramethylpyrylium perchlorate (**8**) also gave two products, but here they were formed sequentially, the 3-ethyl isomer (**9**) being the primary product and the 2-ethyl isomer (**10**) the secondary.

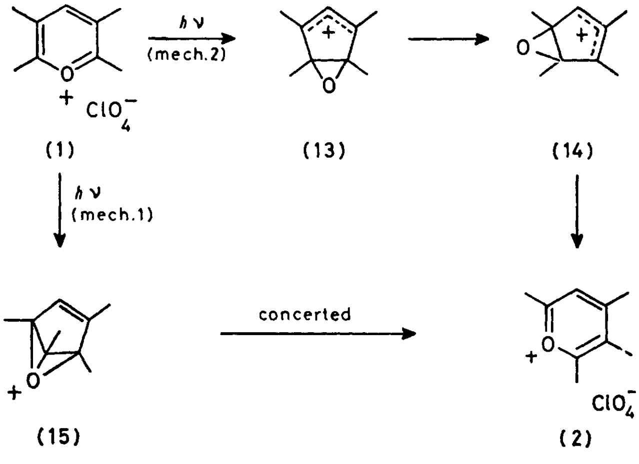
(11)

(12)

Permutation pattern analysis[6] of these reactions restricts the possible transposition modes to (**11**) and (**12**). For a proper discrimination between the two we need an appropriately substituted additional example; however, analogy, in particular with the light-induced 2,6-bonding observed in *N*-alkylpyridinium[7] and 4-hydroxypyrylium cations,[1] and 4-pyrones,[2] leads us at present to favour the permutation pattern (**11**), which denotes a simple interchange of the heteroatom and C(2) or C(6). Such interchanges suggest the intermediacy of 6-oxabicyclo[3.1.0]hexenyl cations, interconverting by walk of the heteroatom [*e.g.* (**1**)→(**13**)→(**14**)→(**2**), *cf.* ref. 2], or of oxoniabenzvalenes, which, rearomatising, could, in principle, yield both the reactant and the transposed product [*e.g.*, (**15**)→(**1**) + (**2**)].

However, such mechanistic formulations must also accommodate the sharply contrasting behaviour of pyrylium cations that, unlike the above cases, lack a 3-and/or a 5-alkyl-group. Thus, irradiation of 2,3,4,6-tetramethylpyrylium perchlorate (**2**) in acetonitrile at 254 or 300 nm gave no sign of transposition, either to (**1**) or to the 2,3,4,5-tetramethyl isomer [< 2%, by n.m.r., when irradiated for 20 times as long as required, under comparable conditions, for a 50% conversion of (**1**)]: the compound decayed very slowly upon prolonged irradiation, but no new n.m.r. signals appeared. Other pyrylium salts totally inert to phototransposition in acetonitrile were 2,4,6-trimethyl-, 4-t-butyl-2,6-dimethyl-, 4-ethyl-2,6-dimethyl-, 2-ethyl-4,6-dimethyl-, 2,6-di-t-butyl-4-methyl-, and 6-ethyl-2,3,4-trimethyl-pyrylium perchlorate. Several of the 2,4,6-trialkyl compounds were also irradiated in other polar, but weakly nucleophilic media [2,2,2-trifluoroethanol, trifluoroacetic acid, concentrated sulphuric acid (with or without added potassium bisulphate), *N*-methylformamide, and propylene carbonate], but with the same result.

The dichotomy between 3,5-dialkylated pyrylium cations and the rest is inexplicable in terms of freely interconverting oxabicyclohexenyl cations or the stepwise rearomatisation of oxoniabenzvalenes *via* oxabicyclohexenyl cations. In the case of (**1**) and (**2**), for example, the relative inductive stabilisations of the positive charges in (**13**) and (**14**) imply that the isomerisation of (**14**) to (**13**) should be faster than the reverse process and that (**15**), the valene common to (**1**) and (**2**), should partition regioselectively to (**13**) (*cf.* ref. 7) and thence to (**1**). Consequently, if excited (**1**) and (**2**) underwent 2,6-bonding or valene formation with comparable efficiencies, the transposition of (**2**) to (**1**) would be expected to occur more readily than the reverse reaction, which is contrary to the facts.‡ The simplest ways of achieving the correct substituent dependendence are as follows.



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† In preparative runs, 25 ml samples of 0·04 mol l^{-1} solutions of (**1**) were used in quartz or Pyrex tubes. For n.m.r. studies, 0·5 ml samples of 0·16 mol l^{-1} solutions in CD_3CN were irradiated directly in n.m.r. tubes; on this scale *ca.* 50% conversion was achieved after 17 h with 300 nm light (Rayonet photochemical reactor). Transposition was slower with 254 nm light, owing to poorer light absorption (2,3,5,6-tetramethylpyrylium perchlorate has λ_{max} 302·5 nm, ϵ 13650). Similar results were obtained upon u.v. irradiation of (**1**) in 2,2,2-trifluoroethanol, methanol, trifluoroacetic acid, and water. Transposition was not quenched by 0·2 M biacetyl (in CD_3CN at λ 300 nm).

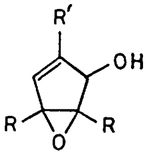
‡ Related models allowing for the probable sensitivity of the rate of bicyclohexenyl rearomatisation to substitution pattern seem no more successful. Rearomatisation would have to be more sensitive to the alkyl-substitution pattern than is the oxygen walk, but the positive charge distributions in pyrylium and oxabicyclohexenyl cations imply the opposite, for an electron-releasing substituent will have a greater stabilising effect at one of the terminal allylic carbons in an oxabicyclohexenyl cation than at the position 2,4, or 6 in a pyrylium cation and, *a fortiori*, in the transition state for rearomatisation.

(i) The primary ground-state photoproduct is an oxoniabenzvalene,§ and this rearomatises thermally in a concerted fashion (*cf.* benzvalene itself[8]). Then, in so far as the transition state for rearomatisation possesses pyrylium character, partition will favour the pyrylium cation with the more stable ground state, *i.e.*, with the greater number of alkyl-groups at positions 2,4, and 6. In these terms, both (**1**) and (**2**) tautomerise photochemically to (**15**), but the outcome is biased strongly in favour of the reactant in the case of (**2**) and the ring-scrambled pyrylium ion in the case of (**1**).

(ii) The primary ground-state photoproduct is an oxabicyclohexenyl cation, but, in order to achieve 2,6-bonding, S_1 ($\pi\pi^*$) of the pyrylium ion must surmount a potential-energy barrier, the height of which is sensitive to the stability of the resultant bicyclohexenyl cation. (*Cf.* recent theoretical discussions of the effects of avoided crossings on the shapes of adiabatic potential-energy surfaces.[9]) The possibility, or otherwise, of transposition might then be governed by the efficiency with which 2,6-bonding is able to compete with other deactivation processes available to S_1. For example, the process S_1 (**1**)→ground-state (**13**) might well be faster than the process S_1 (**2**)→ground-state (**14**). Then, other things being equal, (**1**) transposes normally by the route (**13**)→(**14**)→(**2**), whereas (**2**) fails to transpose because (**14**) is virtually inaccessible from S_1 (**2**) under our reaction conditions.

For either view, the differences in the relevant barrier heights need not be great: to account for a factor of 500, the estimated minimum ratio of the transposition efficiencies of (**1**) and (**2**), requires only 12–16 kJ mol^{-1}.

Further work is required to decide between these alternatives (or to show that the dichotomy has a more subtle, photophysical basis). However, neither hypothesis is inconsistent with the established[3] photochemical reactivity of 2,4,6-trialkylpyrylium cations in water, which also involves S_1. In hypothesis (i), we simply envisage nucleophilic attack by water on the oxoniabenzvalene to give an oxabicyclohexenol (**16**) or similar species, which, under the acidic conditions necessarily prevailing, could yield all the observed[3] photohydration products by simple heterolytic reactions including, for the acyclic keto–aldehydes,[3a,c] C–C bond fission (**17**).¶ In hypothesis (ii), if we exclude the possibility that, in some way, water stabilises oxabicyclohexenyl cations more than other high-polarity solvents do, such as *N*-methylformamide, we might imagine that photohydration involves nucleophilic attack of water directly on the excited pyrylium cation. The attack of water at the β-position of an excited pyrylium cation is unexceptional in the context of aromatic photonucleophilic chemistry[10] and this attack could well be followed by, or even coupled with, 2,6-bonding to give (**16**).[11]



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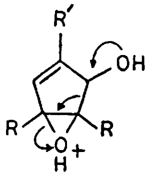

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We gratefully acknowledge financial support of this work by the S.R.C.

(*Received*, 11*th March*, 1980; *Com.* 271.)

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§ A possible variant is that excitation is followed by 2,6-bonding to an *unwalking* oxabicyclohexenyl cation, which then isomerises to the corresponding oxoniabenzvalene. Oxoniabenzvalene formation could then be conceived as competitive with rearomatisation of the bicyclohexenyl cation. This situation would merely bias the overall reaction even more strongly in favour of the more stable pyrylium cation than does the simpler picture envisaged in the text.

¶ The only photohydration product not derivable in this way is a diacetonylcyclopropane formed from 4-t-butyl-2,6-dimethylpyrylium perchlorate (ref. 3b), but this compound has now been shown conclusively to arise solely from 4-t-butylhept-3-ene-2,6-dione, a ground-state hydrolysis product of this pyrylium salt, by a well understood photochemical reaction (M. J. Jorgensen and N. C. Yang, *J. Am. Chem. Soc.*, 1963, **85**, 1698; *cf.* M. J. Jorgensen, *ibid.*, 1969, **91**, 198; *idem, Tetrahedron Lett.*, 1965, 137; M. J. Jorgensen and L. Gundel, *ibid.*, 1968, 4991). The necessity for invoking an initial 1,3-bonding in pyrylium photohydration (ref. 3b) is therefore removed.

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[11] For a recent intramolecular analogy, *cf.* M. Hanaoka, S. Yasuda, K. Nagami, K. Okajima, and T. Imanishi, *Tetrahedron Lett.*, 1979, 3749.