Ring Permutations: a Novel Approach to Aromatic Phototransposition Reactions

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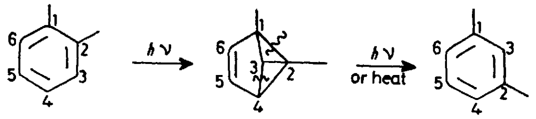
Summary A general problem relating to aromatic phototransposition reactions is defined and analysed in terms of ring-permutation patterns.

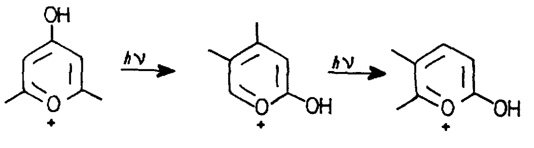
CERTAIN aspects of aromatic photochemistry pose a general problem that has apparently been overlooked in the literature. We define here the problem specifically in relation to certain aromatic photorearrangements and propose an approach to its solution.

It is a commonly held opinion that the phototransposition reactions characteristic of 6-membered aromatic compounds, both homocyclic and heterocyclic, proceed *via* benzvalene or Dewar and prismane intermediates, as exemplified by the photointerconversion of the xylenes [*cf.* equation (1)].[1]



(1)

However, this opinion is more the product of assumption than of rigorous experimental evidence, and it can by no means be regarded as established that it is valid as a general proposition. Indeed, neither the transformation of 3,6-difluoro-4,5-dichloropyridazine into 2,5-difluoro-3,6-dichloropyrazine[2] nor Pavlik's sequence (I) → (II) → (III)[3] can be fitted into this framework. Moreover, the detection of benzvalenes and prismanes as intermediates in aromatic phototranspositions seems to be the exception rather than the rule. Also, apart from Wilzbach and Kaplan's studies of the tri-t-butylbenzenes,[4] there is virtually no case in which any connection at all has been established between the formation of benzvalenes or Dewar and prismane isomers and the occurrence of phototransposition, nor have other conceivable transposition mechanisms (and there are many) been rigorously excluded. All that can be said for certain about, for example, the photoisomerisation of *ortho*- to *meta*-xylene is that C(1) and C(2), initially adjacent, become separated by another ring carbon atom in the product.[5] We do not know that the carbon atom separating C(1) and C(2) in the *meta*-xylene is actually C(3) or the symmetry-related atom C(6), as it would have to be if the benzvalene mechanism were operative. It could, in fact, be C(4) or C(5), neither of which possibilities is consistent with the benzvalene mechanism. Furthermore, even if the carbon atom between C(1) and C(2) was definitely shown to be C(3) or C(6), as demanded by the benzvalene mechanism, we could not regard this mechanism as proven unless we also demonstrated, *inter alia*, that the remaining ring atoms remained unscrambled: a benzvalene mechanism can only interchange a single pair of adjacent atoms. Such indeterminacies are a general feature of known transposition reactions.



(I) (II) (III)

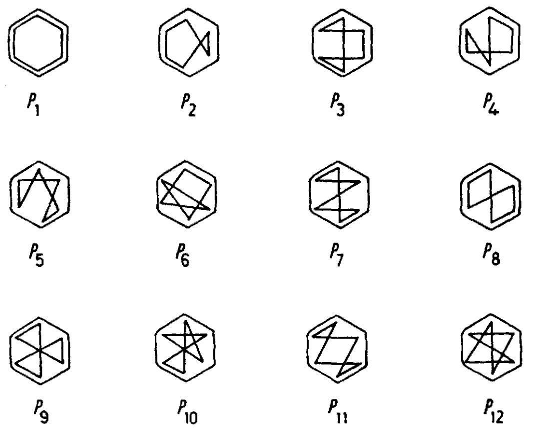
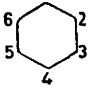


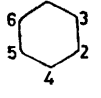
FIGURE. Permutation patterns of a six-membered ring.

We suggest that analysis of such problems is greatly simplified by fixing attention upon the *pattern* of transposition rather than speculating upon the innumerable intermediates that are conceivable. Transposing the atoms in a ring is equivalent to permuting the atoms, and for a 6-membered ring there are 120 permutations, but these reduce to 12 distinct permutation patterns, P_1—P_{12} (see Figure), when different orientations of the patterns within the ring are ignored. In this symbolism, the outer hexagon represents the original connections between the members of the ring, and the internal pattern shows the connections in the transposed product. For example, the transposition of (IV) into (V) is symbolised by P_2 (VI).

Any aromatic transposition reaction in which the fate of all the ring atoms is known can immediately be assigned to one of these patterns. In principle, this requires that each ring atom be distinguishable from the others. When this requirement is not met, it will be impossible to specify a unique permutation pattern. In such cases the reaction pathway must be indeterminate.



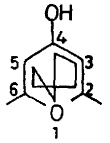
(IV)



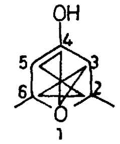
(V)

(VI)

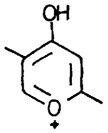
Consider, for example, the transposition (I) → (II) above. Two permutation patterns P_4 (VII) and P_{10} (VIII) will accommodate this result. The indeterminacy arises because the labelling pattern cannot discriminate between ring atoms 2 and 6, or between atoms 3 and 5. However, there is an obvious experiment that resolves this ambiguity, because permutation patterns P_4 and P_{10} applied to the isomeric system (IX) give rise to different (pairs of) products.† This simple example highlights the usefulness of permutation analysis in exposing hitherto unrecognised transposition problems and in facilitating their solution.



(VII)



(VIII)



(IX)

For less heavily substituted cases the possible permutation patterns are legion: the isomerisation of *ortho*- to *meta*-xylene is accounted for by no less than nine. Indeed, our basic general proposition is that *in no case has it been established definitely which of the* 12 *permutations actually occurs in the phototransposition of any* 6-*membered aromatic ring system*. This is because in no case has there been a sufficient number of distinguishing labels on the ring atoms for it to be possible to trace the change in bonding relationships of all six atoms.

We think that it is essential to determine the permutation patterns in aromatic phototranspositions because, even if an unstable entity is detected during the irradiation of an aromatic system, this entity cannot necessarily be accepted as the intermediate in a phototransposition reaction of the aromatic species until it has been shown to be capable of explaining the ring-permutation actually observed. In

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† This analysis presupposes that (i) the endo- and exo-cyclic oxygens do not interchange, (ii) the substituents do not dissociate and recombine (a P_1 process), and (iii) the permutation pathway is independent of the position of methyl substituents.

cases where no unstable entities have been detected—and these cases are in the majority—the present approach has the advantage that, once the permutation pattern in a given transposition reaction is defined, the range of possible intermediates is automatically restricted greatly and the search for them thereby facilitated.

These considerations have implications for many other classes of molecular rearrangement, *inter alia*, those involving cycloheptatrienes,[6] cyclo-octatetraenes,[7] and other $[CH]_n$ systems.[8]

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[1] R. B. Cundall and A. J. R. Voss, *Chem. Comm.*, 1968, 902; D. Anderson, *J. Phys. Chem.*, 1970, **74**, 1686.

[2] D. W. Johnson, V. Austel, R. S. Feld, and D. M. Lemal, *J. Amer. Chem. Soc.*, 1970, **92**, 7505.

[3] J. W. Pavlik and E. L. Clennan, *J. Amer. Chem. Soc.*, 1973, **95**, 1697.

[4] I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1968, **90**, 5868.

[5] By analogy with the study of ring-labelled mesitylene (L. Kaplan, K. E. Wilzbach, W. G. Brown, and Shü Shu Yang, *J. Amer. Chem. Soc.*, 1965, **87**, 675), we assume here that the alkyl groups do not dissociate and recombine.

[6] J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, 1966, **88**, 2494; 1965, **87**, 2751, 2752; R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781; 'The Conservation of Orbital Symmetry,' Academic Press, Weinheim Bergstr., Germany, 1970, p. 134.

[7] L. A. Paquette, M. Oku, W. E. Heyd, and R. H. Meisinger, *J. Amer. Chem. Soc.*, 1974, **96**, 5815. Of the 202 distinct permutation patterns for an eight-membered ring, a large number still remain to be excluded for the thermally induced degenerate skeletal rearrangements of cyclo-octatetraenes, despite the detailed study of the reaction in this paper.

[8] *E.g.*, S. Masamune and N. Darby, *Accounts Chem. Res.*, 1972, **5**, 272.