Permutation Patterns and the Phototranspositions of 2-Cyanopyrroles

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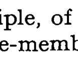
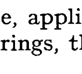
Summary The permutation patterns followed in the phototransposition of 2-cyano- to 3-cyanopyrroles have been defined and show that the nitrogen atom and C(5) interchange in the reaction; a mechanism involving initial 2,5-bonding followed by a skeletal rearrangement is proposed.

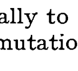
We have recently discussed the phototransposition reactions of 6-membered rings in terms of permutation patterns[1] and applied this approach to the analysis of phototranspositions in the hydroxypyrylium series.[2] This principle, of course, applies equally to phototranspositions in five-membered rings, the permutation patterns of which are shown in (**1**)—(**4**). This communication reports its further application to cyanopyrroles.



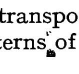
P_1
(**1**)



P_2
(**2**)



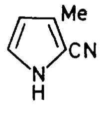
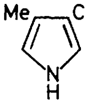
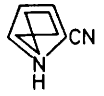
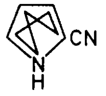
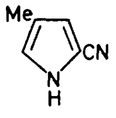
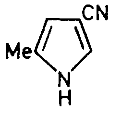
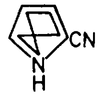
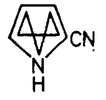
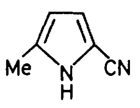
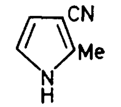
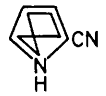
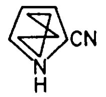
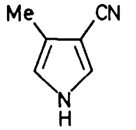
P_3
(**3**)



P_4
(**4**)

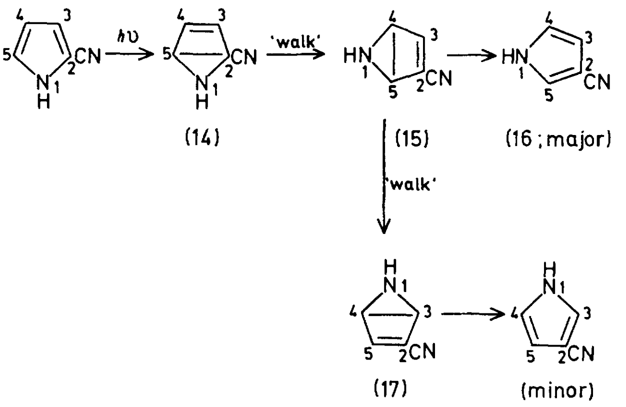
Hiraoka[3] has shown that 2-cyanopyrrole and its *N*-methyl analogue rearrange photochemically to the corresponding 3-cyano isomers. Even with the reasonable assumption that the bond between the cyano group and its ring carbon atom is preserved during the transposition, the results can be accommodated by P_4, by two differently oriented versions of P_2 and three of P_3. The indeterminacy arises owing to the indistinguishability of the unsubstituted ring carbon atoms. We have therefore irradiated† the three methylated 2-cyanopyrroles (**5**)—(**7**) and obtained rearranged products as shown in the Table. Yields were good (20—60%) and no other isomers could be detected (g.l.c. and n.m.r. spectroscopy).

TABLE. Products and permutation patterns in 2-cyanopyrrole phototranspositions

Reactant	Product(s)	Possible permutation patterns	
 (5)		 P_2	 P_3 (9)
 (6)		 P_2	 P_3 (10)
 (7)	 (major)[a]	 P_2	 P_3 (11)
	 (minor)[a] (8)	 P_3 (12)	 P_4 (13)

[a] In a ratio of 30:1.

If we make the reasonable assumption that the methyl groups are a trivial mechanistic perturbation, *i.e.*, that the dominant photochemical process is the same for all three reactants, and if we further assume that methyl and cyano groups serve as positional labels for the ring carbon atoms, then it is apparent from the Table that the permutation pattern common to the major products from (**5**)—(**7**) is P_2 oriented as shown. Note that the three P_3 permutation patterns (**9**)—(**11**) are not identical, being distinguished by virtue of their different orientations with respect to the ring nitrogen atom.



SCHEME

A simple mechanistic scheme consistent with the above observations is shown in the Scheme, in which 2,5-bonding to give (**14**) is followed by a 1,3-sigmatropic shift ('walk') of the nitrogen atom to give (**15**) which can then aromatize to the P_2 product (**16**). Isolation of the product (**8**) from the irradiation of (**7**) is readily accommodated by this mechanism if a small proportion of molecules of the species (**15**) undergo another 'walk' [to (**17**)] before aromatising. This double 'walk' would imply that (**8**) is the product of P_3 permutation (**12**) of (**7**), rather than P_4 (**13**). This point remains to be established by a further labelling study. The suggestion that 2,5-bonding in excited pyrrole initiates the transposition is supported by a correlation diagram for the π,π^* state of pyrrole, and has some experimental support in the work of Hiraoka.[3]

Results conforming to a P_2 permutation pattern have also been obtained for alkylated imidazoles by Beak and Messer,[4] who made similar mechanistic proposals. It is interesting to note that furans and thiophens, so similar to pyrroles in their ground state reactions, should follow such different mechanisms for ring transpositions in the excited state.[5]

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† The pyrroles were irradiated as $1{\cdot}5 \times 10^{-3}$M solutions in acetonitrile with 254 nm light in a Rayonet reactor.

[1] J. A. Barltrop and A. C. Day, *J.C.S. Chem. Comm.*, 1975, 177.
[2] J. A. Barltrop, R. Carder, A. C. Day, J. R. Harding, and C. J. Samuel, *J.C.S. Chem. Comm*, in the press.
[3] H. Hiraoka, *Chem. Comm.*, 1970, 1306; 1971, 1610.
[4] P. Beak and W. R. Messer, *Tetrahedron*, 1969, 25, 3287.
[5] A. Lablache-Combier and M. A. Remy, *Bull. Soc. chim. France*, 1971, 679.