Transpositions in Aromatic Rings

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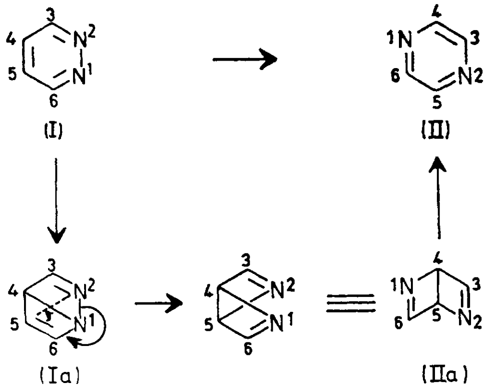
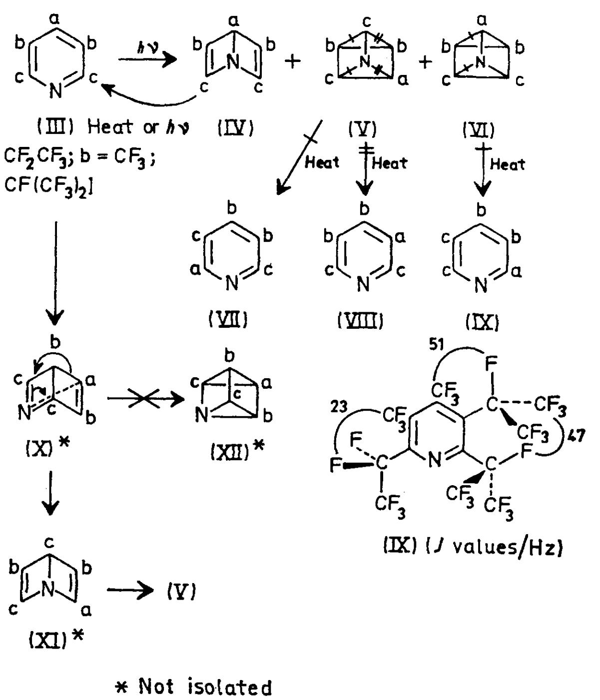
Summary. Photolysis of substituent-labelled perfluoroalkylpyridines gives stable azaprismane derivatives whose structures were established by re-aromatisation; transpositions of the pyridine ring occur and rearrangement of intermediate unsymmetrical *para*-bonded species is indicated.

In a recent communication Barltrop and Day[1] stressed the danger of acceptance of facile mechanisms involving valence isomers for transpositions of aromatic rings and presented a useful notation for transposition patterns for these systems. They are mistaken, however, in claiming that there is virtually no case in which any connection has been established between Dewar and prismane isomers and the occurrence of phototransposition. We have, for example, isolated valence isomers[2,3] corresponding to (Ia) and (IIa) in the photorearrangement of perfluoroalkyl-pyridazines (I) to -pyrazines (II)[4] and demonstrated each step of the conversion. The intermediacy of valence isomers in photorearrangements of perfluoroalkylbenzenes has also been quite clearly demonstrated by Haszeldine and his coworkers.[5]



It was also claimed[1] that in no case has it been established definitely which of the twelve possible permutations actually occurs in the phototransposition of any six-membered aromatic ring system. We consider that the experiments referred to above, including separate substituent labelling of the 4,5- and 3,5-positions in (I),[4] constitute such a case.[6]



Scheme

We now present evidence for the type of rearrangement process represented by (Ia) → (IIa), taking place in the pyridine system. Compound (III)[7] provides an unusually highly substituent-labelled six-membered aromatic ring and photolysis at 254 nm (in $CF_2ClCFCl_2$) gave quantitative conversion into a mixture containing a small amount of a *para*-bonded species (IV) (see Scheme) (C=C stretch at 1693 cm^{-1}), and two azaprismane derivatives (V) and (VI) in approximately equal amounts. Components (V) and (VI) could not be separated completely from each other but samples enriched in (V) or (VI) were obtained by distillation. The azaprismane structures follow from the u.v. and i.r. data, in comparison with data for (III) and (IV), while ^{19}F n.m.r. spectra indicated unsymmetrical and symmetrical structures for (V) and (VI) respectively. Consistent with earlier studies,[8] which established, *e.g.*, that perfluoropentaethylpyridine gives a remarkably stable azaprismane on photolysis, (V) and (VI) could be only slowly converted, at 175°, into the pyridines (VII)—(IX), which were separated by g.l.c. Using mixtures of (V) and (VI) of varying composition, it was possible to demonstrate that the azaprismane (VI) leads to the pyridine (IX) while (V) gives a mixture of both pyridines (VII) and (VIII). The structures of the pyridines (VII)—(IX) followed simply from the ^{19}F n.m.r. spectra, since perfluoroalkyl groups adopt preferential conformations in these systems,[7] and the coupling shown for (IX) establishes its structure unambiguously. Similarly, the structures of (VII) and (VIII) are equally clear.

It is clear how the symmetrical azaprismane (VI) may lead to only one pyridine derivative (IX) (see Scheme), but the only azaprismane derivative which can lead, specifically, to a mixture of the pyridines (VII) and (VIII) is structure (V), by rearomatisation in the manner shown.

There then remains the problem of a process for forming (V). In principle (XI), and then (V), could be obtained by rearrangement of (IV), but (IV) can be converted quantitatively, by photolysis, into (III), before forming (V). Therefore, we suggest the formation of an unsymmetrical *para*-bonded species (X), which then rearranges to relieve crowding, giving (XI), from which the unsymmetrical azaprismane derivative (V) can be produced. So far, however, we have not isolated any (X) or (XI), although there are some very minor components which we have not identified.

While these reactions, overall, involve a photolytic rearrangement, followed by a pyrolytic rearomatisation, they link with phototranspositions of some pyridines[9] where intermediates corresponding to (VI) and (XII) have been postulated, although not isolated, and this will be discussed elsewhere.

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