# The Fluoride Ion-catalysed Rearrangement of 3,6-Difluoro-4,5-bisheptafluoroisopropylpyridazine†

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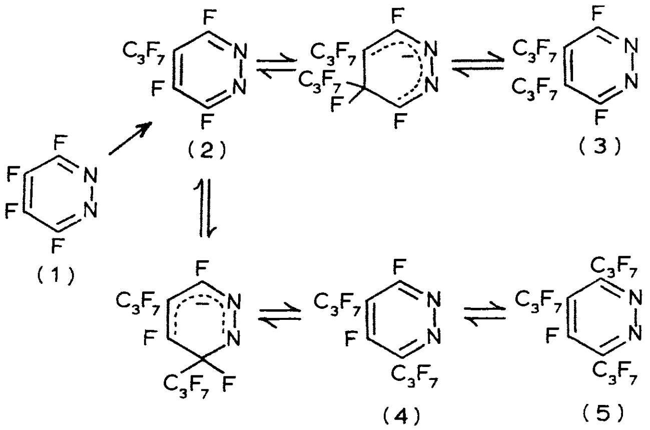
*Summary* The rearrangement of the 4,5- to 4,6-bisheptafluoroisopropylpyridazine (3) → (4) in the presence of fluoride ion is reported, and the importance of this reaction in the formation of the trisheptafluoroisopropyl derivative (5) is indicated.

IN previous publications[1,2] from this laboratory we have described a process for polyfluoroalkylation of aromatic systems including pentafluoropyridine and tetrafluoropyridazine.[3] We have also described an interesting fluoride ion-induced rearrangement[4] of perfluoro-(2,4,5-tri-isopropylpyridine) giving the 2,4,6-substituted pyridine, and novel photochemical and thermal rearrangements[3] of tetrafluoropyridazine (1) and its derivative (3) to corresponding pyrazine and pyrimidine systems. Perfluoro-(4,5-di-isopropylpyridazine) (3) was prepared by fluoride ion-induced reaction of hexafluoropropene with tetrafluoropyridazine (1), and at temperatures between 20 and 60° it is the main product. Under more vigorous conditions, *e.g.* 150°, starting with either (1) or (3), a trisubstituted compound§ (5), m.p. 37—38°, $\lambda_{max}$ (cyclohexane) 255·5 and 326·5 nm, is produced, but so far we have been unable to isolate perfluoro(tetraisopropylpyridazine). The formation of the trisubstituted compound (5) indicates a rearrangement, and this was confirmed by direct reaction of (3) with fluoride ion at 150°, when the product contained approximately equal amounts of the rearranged disubstituted derivative (4), b.p. 160°/760 mm Hg, $\lambda_{max}$ (cyclohexane) 255·5 and 323 nm, the monosubstituted derivative (2), b.p. 145°/760 mm, $\lambda_{max}$ (cyclohexane) 261·5, 287, and 307·5 nm, and the trisubstituted derivative (5), together with small amounts of oligomers of hexafluoropropene. This result suggests an intermolecular rearrangement and the overall results are consistent with the scheme showing the reversible addition of perfluoroisopropyl anion. The products isolated depend on whether kinetic or thermodynamic control operates. It has been established[5] that tetrafluoropyridazine (1) is most reactive towards nucleophiles at positions 4 and 5, and clearly crowding between heptafluoroisopropyl groups[6] is relieved in the rearrangement of (3) to (4).



In a recent communication,[7] Haszeldine and his coworkers reported the formation of (5) from (1) or (3). Reference was made to our own work,[4] which has been concerned with these and similar reactions for several years, and which is not based on any other source.

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§ Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds mentioned.

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