The Isomerisation of Perfluoropyridazines to Perfluoropyrimidines and to Perfluoropyrazines

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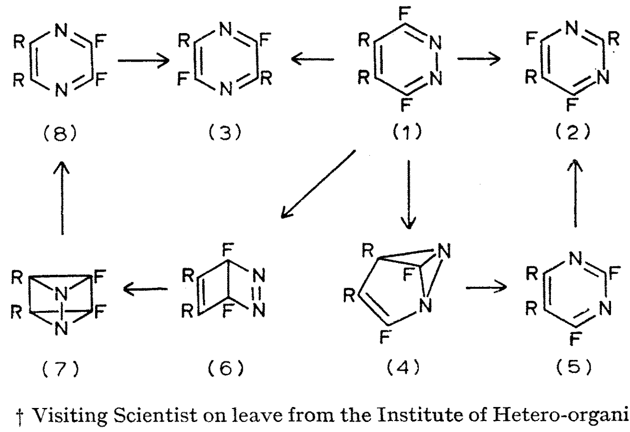
Summary Thermal isomerisation of perfluoropyridazines gives perfluoropyrimidines, but u.v. irradiation gives perfluoropyrazines.

WE report what we believe to be the first isomerisations of the pyridazine ring which indicate the intermediacy of diazabenzvalene and diazaprismane systems.

We found that during the preparation[1] of tetrafluoropyridazine (1; R = F), by reaction between tetrachloropyridazine and potassium fluoride, the product contained tetrafluoropyrimidine (2; R = F) if temperatures above 330° were used. Further, pyrolysis of tetrafluoropyridazine (1; R = F) on silica wool at 820° (contact time *ca.* 40 sec.) gave tetrafluoropyrimidine (2; R = F) in *ca.* 60% yield together with a trace, *ca.* 3%, of the known[2] tetrafluoropyrazine (3; R = F).

In contrast, irradiation of tetrafluoropyridazine (1; R = F) with an unfiltered medium-pressure mercury lamp gave an almost quantitative yield of tetrafluoropyrazine (3; R = F). No tetrafluoropyrimidine (2; R = F) was detected in the photolysis product, while pure samples of (2; R = F) and (3; R = F) were unchanged after similar irradiation.



3,6-Difluoro,4-5-bisheptafluoroisopropylpyridazine (1; R = iso-C_3F_7) m.p. 68—69° λ_{max} (cyclohexane) 277·5 and 285 nm., prepared by polyfluoroalkylation[3] of tetrafluoropyridazine (1; R = F), isomerises on u.v. irradiation to the pyrazine (3; R = iso-C_3F_7) b.p. 142°/760 mm., λ_{max} (ethanol) 281 nm. The same pyrazine (3, R = iso-C_3F_7) was obtained by polyfluoroalkylation of tetrafluoropyrazine (3; R = F). The i.r. and u.v. spectra of the bisheptafluoroisopropyldiazines (1, 2, and 3; R = iso-C_3F_7 in each case) are characteristic of the appropriate diazine ring-system, and the shifts[4] and coupling constants of their ^{19}F n.m.r. spectra indicate the orientations of the substituents; correct analyses and mass spectra have also been obtained for each.

Thermal isomerisation of the bisheptafluoroisopropylpyridazine (1; R = iso-C_3F_7) occurred more readily (560°, 50 sec.) than that of tetrafluoropyridazine (1; R = F) to give 4,6-difluoro-2,5-bisheptafluoroisopropylpyrimidine (2; R = iso-C_3F_7), b.p. 148°/760 mm., λ_{max} (cyclohexane) 148 nm., in *ca.* 50% yield, together with the pyrazine (3; R = iso-C_3F_7), *ca.* 3%, and a third isomeric product, *ca.* 6%, whose structure has not yet been determined.

We suggest that the thermal isomerisation of tetrafluoropyridazine (1; R = F) proceeds through tetrafluorodiazabenzvalene (4; R = F) by fission of the N–N bond and re-aromatisation to tetrafluoropyrimidine (2; or 5; R = F). Thermal isomerisation of the bisheptafluoroisopropylpyridazine (1; R = iso-C_3F_7) would then give the 4,5-bisheptafluoroisopropylpyrimidine (5; R = iso-C_3F_7), *via* (4; R = iso-C_3F_7); it is probable that the principal isolated product (2; R = iso-C_3F_7) results from isomerisation of this initial product (5; R = iso-C_3F_7) by an anionic rearrangement similar to that which occurs in the isomerisation of 2,4,5-trisheptafluoroisopropylpyridine.[5]

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The different course of photochemical isomerisation of tetrafluoropyridazine probably occurs through the tetrafluorodiazaprismane[6] (7; R = F), presumably formed *via* the Dewar-benzene analogue (6; R = F), followed by fission of the N–N bond and re-aromatisation to tetrafluoropyrazine (3 and 8; R = F). Since no tetrafluoropyrimidine (3; R = F) could be detected in the photolysis product, although it is stable to the experimental conditions, it is unlikely that the diazabenzvalene (4; R = F) is involved in the photochemical reaction. Photo-isomerisation of the bisheptafluoroisopropylpyridazine (1; R = iso-C_3F_7) would be expected to give (8; R = iso-C_3F_7) and, as before, we suggest that the initial product (8; R = iso-C_3F_7) isomerises by an anionic rearrangement[5] to the observed *para*-substituted pyrazine (3; R = iso-C_3F_7).

The high yields obtained in these isomerisations contrast with those obtained in the only previously reported isomerisations of a diazine system, when pyrazines were converted thermally,[7] or photochemically,[8,9] to pyrimidines in very low yield. We are encouraged to suggest the intermediacy of (4, 6, and 7) by the recent isolation of surprisingly stable isomers of perfluoro(alkylbenzenes)[10,11] as well as that of the less stable hexafluorobicyclo[2,2,0]hexa-2,5-diene.[12]

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