Thermal Rearrangements of Fluorinated Pyridazines: Mechanism

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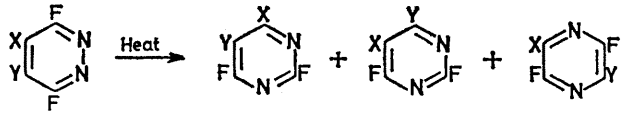
Summary Experiments involving substituent and ^{15}N labelling have ruled out cycloaddition and/or fragmentation mechanisms for the thermal transformation of perfluoroalkylpyridazines to mainly the corresponding pyrimidine derivatives.

WE have observed previously novel thermal transformations of the fluorinated pyridazines (**1** and **2**) to, predominantly, the corresponding pyrimidines (**1a**), (**2a**) and (**2b**), and also some of the pyrazine derivative (**1c**).[1] We concluded that these transformations, carried out in a flow of nitrogen,



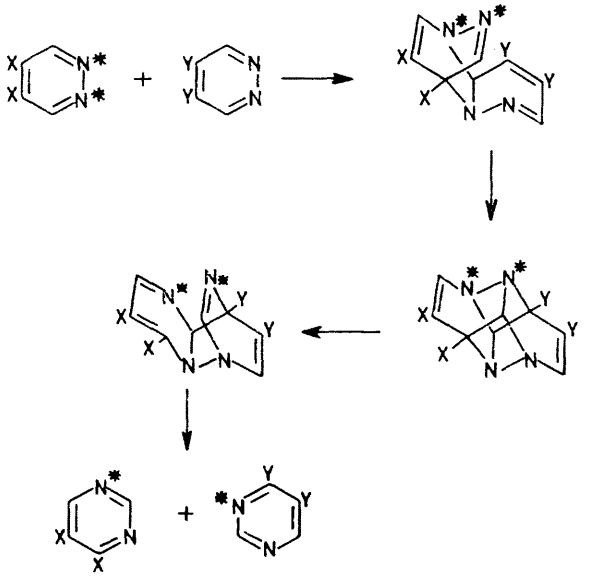
(1), X=Y=CF(CF$_3$)$_2$	(1a)			+	(1c)
(2), X=F; Y=CF(CF$_3$)$_2$	(2a)	+	(2b)		
(3), X=Y=CF(CF$_3$)C$_2$F$_5$	(3a)			+	(3c)
(4), X=F; Y=CF(CF$_3$)C$_2$F$_5$	(4a)	+	(4b)		
(5), X=CF(CF$_3$)$_2$; Y=CF(CF$_3$)C$_2$F$_5$	(5a)	+	(5b)	+	(5c)

All transformations are essentially quantitative

involved the intermediacy and rearrangement of diazabenzvalene derivatives and unimolecular processes were assumed because the same products were obtained under high vacuum, albeit at higher temperatures. Nevertheless Mahler and Fukunaga have obtained some interesting metathesis reactions under static conditions, *e.g.* equilibration of perchlorodiazines at 550 °C in a gold tube,[2] and these workers suggested that cycloaddition mechanisms for transpositions in aromatic systems could be important, depending on pressure.

We established that the perfluorodi-isopropylpyridazine (**1**) will rearrange in a sealed tube at 350 °C[1] and we now find that the perfluorodi-s-butylpyridazine (**3**) will rearrange even more efficiently under these conditions, or at lower temperatures. It was possible, therefore, that these sealed tube processes could involve unusually easy cycloadditions, similar to those described by Mahler and Fukunaga. However, we have now ruled out this possibility by showing that cross-over products do not occur, either involving exchange of perfluoroalkyl substituents or of nitrogen atoms. Mixtures containing compounds (**1**) + (**3**) and (**2**) + (**4**) were heated at 350 and 400 °C, respectively in sealed tubes, *i.e.* conditions under which the individual compounds rearranged to products. There was no evidence in the product of compounds arising from exchange of perfluoroalkyl groups between compounds (**1**) and (**3**) or

between (**2**) and (**4**). As a further test of exchange of perfluoroalkyl groups, compound (**5**) was synthesised by reaction of (**4**) with hexafluoropropene and caesium fluoride.[3] Heating of compound (**5**) at 300 °C in a sealed tube gave compounds (**5a**—**c**) with no trace of products containing two perfluoroisopropyl, or two perfluoro-s-butyl groups, *i.e.* cross-over products.



SCHEME. All unmarked bonds to fluorine

A cycloaddition mechanism, as shown in the Scheme, would exchange nitrogen atoms but not substituent groups and, at least the main products, *i.e.* pyrimidines, could be accounted for in this way. However, we have been able to synthesise a sample of the perfluorodi-isopropylpyridazine (**1**), doubly labelled with ^{15}N, starting with a sample of hydrazine containing 95·4% ^{15}N. Reaction of the hydrazine with dichloromaleic anhydride followed by reaction of the product with phosphorus trichloride oxide gave labelled tetrachloropyridazine. This was converted into a sample of (**1**), using established procedures,[3,4] and then diluted with unlabelled (**1**) (50:50). The sample of (**1**) was mixed with excess (5:1) of (**3**) and the mixture heated. The product was analysed by m.s.–g.l.c. and, for (**1a**) in the mixture, the mass spectra showed peaks at *m/e* 452 (corresponding to M^+) and 454 (corresponding to $M^+ + 2$). Obviously, no exchange of nitrogen atoms had occurred, otherwise a peak would have been observed at 453 (corresponding to $M^+ + 1$) as indicated by the Scheme.

Therefore, for these thermal transformations, even using a static system, we have eliminated any mechanism involving intermolecular exchange of groups or atoms. This rules out mechanisms involving fragmentation and/or cycloaddition processes and gives added substance to our original suggestion[1] of the intermediacy of diazabenzvalenes, to account for these novel and highly specific transformations.

(*Received*, 29*th January* 1979; *Com.* 079.)

[1] R. D. Chambers, M. Clark, J. R. Maslakiewicz, W. K. R. Musgrave, and P. G. Urben, *J.C.S. Perkin I*, 1974, 1513.
[2] W. Mahler and T. Fukunaga, *J.C.S. Chem. Comm.*, 1977, 307.
[3] S. L. Bell, R. D. Chambers, M. Y. Gribble, and J. R. Maslakiewicz, *J.C.S. Perkin I*, 1973, 1716.
[4] R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc.* (*C*), 1968, 2116.