

PYRIDAZINE REARRANGEMENTS

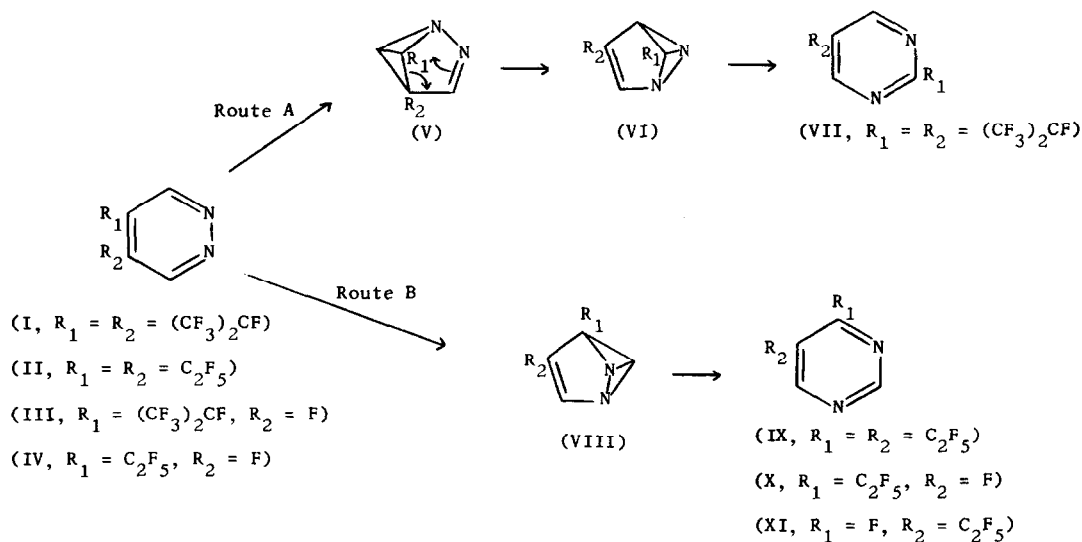
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We have previously described<sup>1</sup> a novel thermal rearrangement of perfluoro-4,5-di-isopropylpyridazine (I) to give perfluoro-2,5-di-isopropylpyrimidine (VII) i.e. a reaction in which a change in the relative positions of the perfluoroalkyl groups, as well as the nitrogen atoms, occurs. We now report a rearrangement of perfluoro-4,5-diethylpyridazine (II)<sup>2</sup> to perfluoro-4,5-diethylpyrimidine (IX) where, in contrast to the pyrolysis of (I), the relative position of the pentafluoroethyl groups remains unchanged.

Pyridazine (II) was pyrolysed at 650° in a stream of dry nitrogen (contact time ca. 60 secs.) giving the pyrimidine (IX) (60% yield) in which the positions of the substituents were easily deduced from the <sup>19</sup>F n.m.r. spectrum.

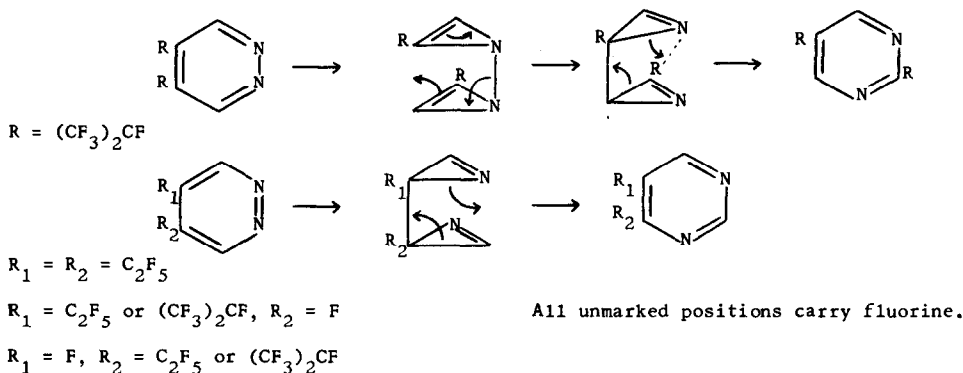


All unmarked positions carry fluorine.

We have previously interpreted<sup>1</sup> the formation of (VII) on the basis of the intermediacy of diazabenzvalene (V) and its preferential rearrangement to separate bulky

perfluoroisopropyl groups i.e. (V)  $\rightarrow$  (VI), followed by a rearomatization which separates nitrogen atoms (Route A). The formation of (IX) from (II) suggests that separation of the perfluoroalkyl groups is no longer the primary process, the driving force being separation of the nitrogen atoms (Route B) via only one diazabenzvalene intermediate (VIII). Also, reactions of both the perfluoro-isopropyl (III) and -ethyl (IV) derivatives corresponded with Route B rather than Route A. Perfluoro-4-isopropylpyridazine (III) gave a mixture of perfluoroalkylpyrimidines with the perfluoroalkyl group at the 4- or 5-positions but not at the 2-position. Likewise, the pentafluoroethyl derivative (IV) gave a mixture of the pyrimidines (X) and (XI).

There is, however, an alternative rationalization of these results which, so far, we have not considered, i.e. involving formation and sigmatropic rearrangements of the, perhaps less likely, diazabicyclopropenyls. The observed products from our pyrolysis reactions could be accounted for as shown below.



Clearly, it would be possible to produce any isomer after the appropriate number of steps but the observed products occur earlier along the reaction path, similar to the scheme involving diazabenzvalenes, suggested earlier.<sup>1</sup> Relevant to this possibility is the report of thermal rearrangements of phenyl derivatives of bicyclopropenyl to the corresponding benzenes.<sup>3</sup> As yet we are unable to distinguish between these processes.

#### REFERENCES

1. R.D. Chambers, J.A.H. MacBride and W.K.R. Musgrave, *J. Chem. Soc. (C)*, 1971, 3384.
2. R.D. Chambers, R.P. Corbally, M.Y. Gribble, and W.K.R. Musgrave, *Chem. Comm.*, 1971, 1345.
3. R. Breslow, P. Gal, H.W. Chang, and L.J. Altman, *J. Amer. Chem. Soc.*, 1965, 5139.