

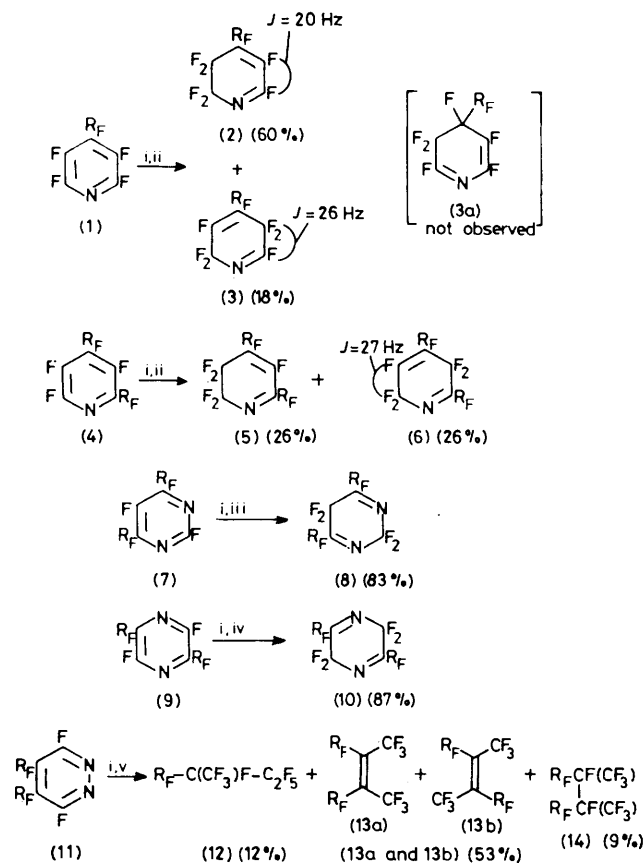
Perfluoro-aza- and -diaza-cyclohexadiene Derivatives

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Summary Fluorinations of perfluoroalkyl-pyridines, -pyrimidines, or -pyrazines with $\text{CoF}_3\text{-CaF}_2$ give good yields of the corresponding cyclic aza- or diaza-dienes; per-

fluoroalkylpyridazines give products which involve loss of nitrogen.

PERFLUOROALKYL derivatives of azines and diazines are now readily available through fluoride ion induced reactions of perfluoroalkenes with the corresponding aromatic compound.¹ Fluorinated aza- or diaza-alkenes are not readily available, but we now find that fluorination of perfluoroalkyl-azines or -diazines over a mixture of cobalt trifluoride with calcium fluoride gives diene derivatives as the main products in high yields. This is in contrast to the corresponding fluorination of pyridine, where low yields of cyclic products are obtained,² or even pentafluoropyridine where some fragmentation occurs.³



i, CoF_3 ; ii, 118°C ; iii, 172°C ; iv, 156°C ; v, 163°C . $\text{R}_F = \text{CF}(\text{CF}_3)_2$.

Fluorination of the pyridine derivatives (1) and (4) in each case gave a mixture of the corresponding 1-aza-1,3-, and 1-aza-1,4-cyclohexadienes (2) and (5) and (3) and (6), respectively. The diazine derivatives (7) and (9) each gave a single product (8) and (10), respectively.

Structures of the products follow mainly from the corresponding ^{19}F n.m.r. spectra, on the basis of some well-established points. In all cases the perfluoroalkyl group in the cyclic aza- and diaza-dienes is attached to an unsaturated carbon atom; this follows from the fact that a signal associated with $\text{R}_F\text{-C-F}$ occurs at characteristically high field, while a signal corresponding to N=C-F occurs at characteristically low field.^{3,4} In addition to the perfluoroalkyl group the ^{19}F n.m.r. spectrum of (2) showed signals corresponding to one fluorine atom at 53 and 108 p.p.m. and signals corresponding to two fluorine atoms at 103 and 115 p.p.m. while (3) showed corresponding signals at 58, 110 (int. 1) and 88, 103 (int. 2) p.p.m. In contrast, compounds (5) and (6) showed no low-field resonance, the signals corresponding to one fluorine atom occurring at 101 and 102 p.p.m. More detailed analysis of the ^{19}F n.m.r. spectra confirmed these assignments. Structures of the diaza-dienes (8) and (10) followed even more simply from the fact that neither structure contained a perfluoroalkyl group attached at a saturated position.

It is interesting that the products obtained from fluorination of the pyridine derivatives (1) and (4) contained none of the 2-aza-diene derivatives, *e.g.* (3a). However, the fact is that wherever the possibility of either $\text{R}_F\text{C=C}$ or FC=C as an element of structure arises, the former occurs exclusively. Therefore, the absence of structures like (3a) is probably a consequence of the higher energy of systems containing fluorine atoms directly attached to the double bond. This seems to be a further example of an effect arising from electron pair- π -bond repulsion involving fluorine atoms attached directly to a double bond.⁵

Reactions of the pyridazine derivative (11) led exclusively to a loss of nitrogen and the products (12)–(14) were obtained.

The chemistry of these unusual aza- and diaza-dienes is being explored and preliminary results on photochemically induced rearrangements are described in the following communication.⁶

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¹ R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley-Interscience, New York, 1973, p. 296, and references therein.

² P. L. Coe, J. C. Tatlow, and M. Wyatt, *J.C.S. Perkin I*, 1974, 1732, and references therein.

³ R. D. Chambers, D. T. Clark, T. F. Holmes, W. K. R. Musgrave, and I. Ritchie, *J.C.S. Perkin I*, 1974, 114.

⁴ R. D. Chambers, J. R. Maslakiewicz, and K. C. Srivastava, *J.C.S. Perkin I*, 1975, 1130.

⁵ Ref. 1, p. 144.

⁶ R. D. Chambers, R. D. Hercliffe, and R. Middleton, following communication.