

Photochemical Conversions of some Fluorinated Aza- and Diaza-cyclohexadienes

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Summary Products obtained from the photolysis of perfluorinated derivatives of aza- and diaza-cyclohexadienes show that a variety of skeletal processes occur

including ring-opening, fluorine migration, and retro-Diels-Alder reactions.

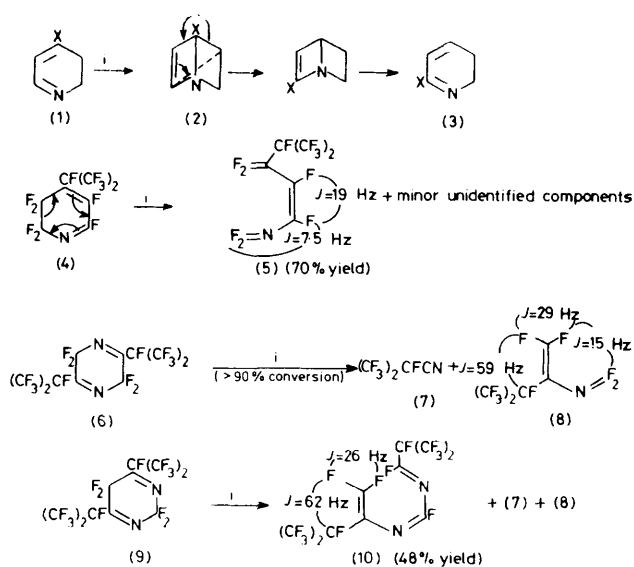
FLUORINE and perfluoroalkyl groups are being used successfully as substituent labels for the study of skeletal rearrangements in aromatic systems.^{1,2} We have now investigated the photolysis of some fluorinated aza- and diaza-cyclohexadienes because, in principle, rearrangement of *e.g.* (1) → (3) could occur. Such a process would be analogous to the one which has been observed for the *para*-bonded isomers of fluorinated pyridazines³ and postulated to explain the results of photochemically induced rearrangements of some fluorinated pyridines.²

Irradiation of the diene (4) gave total conversion into a product mixture containing mainly (5), together with some minor components which have not yet been characterised. The structure (5) is deduced from spectroscopic data: ¹⁹F n.m.r. δ 96.1, 113.8, 114.3, and 136.7 p.p.m., from CFCl₃ (CF=C) and two broad signals at 32.9 and 51.2 p.p.m. (typical of -N=CF₂); ν_{max} 1680, 1767, and 1775 cm⁻¹ (C=C and C=N stretch). The stereochemistry follows from the magnitude of the coupling constants⁴ which are shown in the Scheme.

For comparison, the diaza-systems (6) and (9) were irradiated under comparable conditions. The derivative (6) gave a > 90% conversion into an equimolar mixture† of perfluoroisobutyronitrile (7) and a new compound (8). The structure of (8) follows from spectroscopic data: ¹⁹F n.m.r. δ 83.1 and 93.0 p.p.m. (CF₂=C) and broad signals at 42.6 and 55.9 p.p.m. (N=CF₂); ν_{max} 1805 and 1732 cm⁻¹ (C=N and C=C stretch).

The product mixture† (76% conversion) from (9) is more complicated; compounds (7) and (8) were obtained in approximately equimolar amounts, together with the major product (10). The structure of (10) follows simply from the spectroscopic data: ¹⁹F n.m.r. δ 41.8 (int. × 2) (N=CF), 77.7, and 91.3 p.p.m. (C=CF); ν_{max} 1678, 1731, and 1799 cm⁻¹ (C=N and C=C stretch).

The formation of (5) is consistent with the well documented formation of trienes from cyclohexa-1,3-dienes⁵



SCHEME i, 253.7 nm, vapour phase (Hg); for syntheses of (4), (6), and (9), see preceding communication.

but contrasts with the formation of a bicyclo[2.2.0]hex-2-ene from perfluorocyclohexa-1,3-diene.⁶ Obviously, we are unable, at this preliminary stage, to comment on the detailed mechanisms of these transformations but formation of (7) and (8) from either (6) or (9) represents rare examples of photochemically induced retro-Diels-Alder reactions, while formation of (10) from (9) must involve a migration of fluorine. These new examples illustrate the gradually increasing range of skeletal processes which may be studied through fluorocarbon systems.

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† All product mixtures were separated by preparative-scale v.p.c. and the new compounds reported were each characterised individually, giving satisfactory elemental analysis and/or corresponding parent peak in the mass spectrum.

¹ R. D. Chambers and R. Middleton, *J.C.S. Chem. Comm.*, 1977, 154.

² R. D. Chambers and R. Middleton, *J.C.S. Perkin I*, 1977, 1500, and references therein.

³ R. D. Chambers, J. R. Maslakiewicz, and K. C. Srivastava, *J.C.S. Perkin I*, 1975, 1130.

⁴ J. W. Emsley, L. Phillips, and V. Wray, *Progr. N.M.R. Spectroscopy*, 1976, **10**, 83; R. E. Banks, 'Fluorocarbons and their Derivatives', Macdonald, London, 1970, 233.

⁵ A. Padwa, L. Brodsky, and S. C. Clough, *Chem. Comm.*, 1971, 417.

⁶ W. J. Feast, W. K. R. Musgrave, and R. G. Weston, *Chem. Comm.*, 1970, 1337.