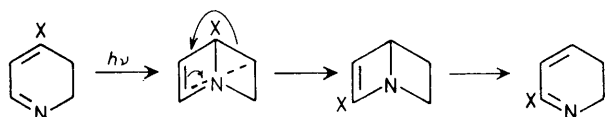


## Photochemistry of Halogenocarbon Compounds. Part 4.<sup>1,2</sup> Photochemical Conversions of Some Fluorinated Aza- and Diaza-cyclohexadienes

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Photoreaction of perfluoro-4-isopropyl-1-azacyclohexa-1,3-diene (1) gives a cyclobutene derivative (4), apparently *via* ring opening to an azatriene. Similarly, the perfluoro-di-isopropyldiazacyclohexa-1,4-dienes (7) and (10) undergo a retro [ $\pi$ ,4 +  $\pi$ ,2] process and, in one case, a diazatriene (11) was isolated. Conversions of some apparently similar systems did not occur.

FLUORINE and perfluoroalkyl groups are being used successfully as substituent labels for the study of skeletal rearrangements in aromatic systems.<sup>3,4</sup> In our earlier studies, we clearly established an unusual mechanism for photochemically induced 1,3-shifts in fluorinated pyridazines,<sup>5</sup> involving *para*-bonded intermediates, and a similar process probably occurs in the irradiation of some fluorinated pyridines.<sup>1</sup> We have now investigated the irradiation of some aza- and diaza-cyclohexadienes: in principle, the process shown in the Scheme could occur since it is analogous to the rearrangement of *para*-bonded isomers of fluorinated pyridazines.

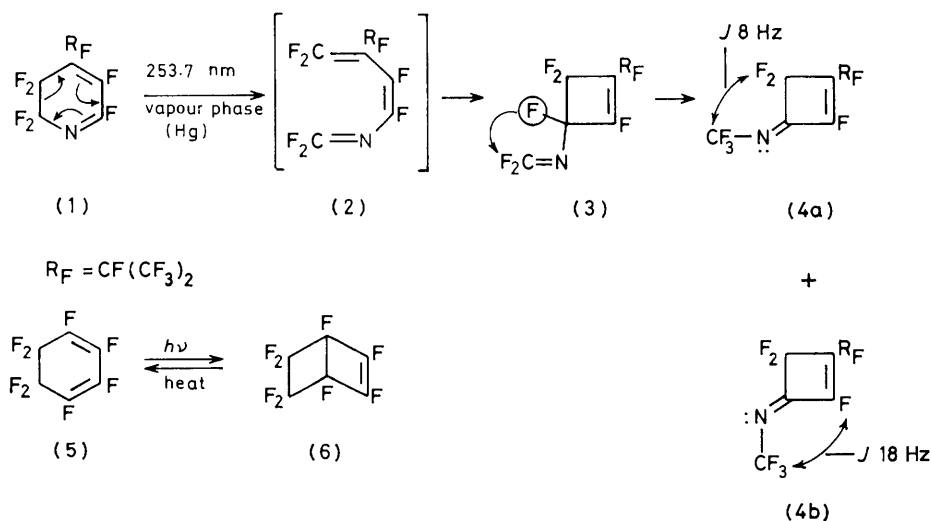


SCHEME

Various aza- and diaza-cyclohexadienes have now been synthesised from corresponding fluorinated aromatic derivatives, by further fluorination over cobalt trifluoride,<sup>6,7</sup> and the starting materials described in the present publication have been obtained using this procedure. Irradiation of the diene (1) gave a compound (4) which exists as a mixture of isomers (4a and b). The

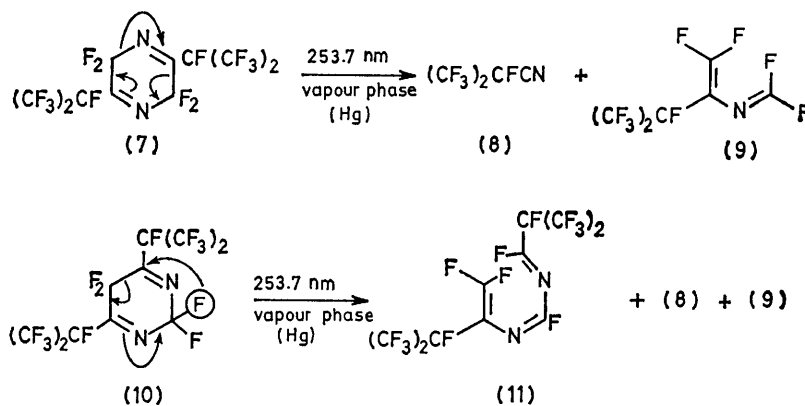
structure of (4) follows from the <sup>19</sup>F n.m.r. data and an isomer ratio of 2 : 1 [(4a) : (4b)] is indicated. Chemical shifts and integrated intensities reveal that each isomer contains CF<sub>3</sub>-N, CF<sub>2</sub>, and CF=. Furthermore, a coupling of 8 Hz between CF<sub>3</sub>-N and adjacent CF<sub>2</sub> in the isomer (4a) distinguishes this isomer from (4b), where a corresponding coupling of 18 Hz between CF<sub>3</sub>-N and CF= occurs. Geometric isomerism arising from the stereochemical integrity of nitrogen in fluorocarbon imines is well known,<sup>8,9</sup> and the barriers to inversion are now thought to be influenced mainly by steric effects.<sup>8</sup> Surprisingly, heating a mixture of (4a) and (4b) up to 90 °C did not result in any coalescence of the <sup>19</sup>F n.m.r. signals but the barrier to inversion of nitrogen in an imine might well be affected by incorporation of the carbon of the imine group into a four-membered ring.

In an earlier experiment,<sup>2</sup> irradiation of (1) gave as the major product a compound to which we assigned structure (2), but it now seems more likely that this was in fact compound (3). However, in subsequent repeats of this process the major product has always been (4); the compound obtained previously was also isolated but only in minor proportions. We now assign structure (3) to this compound, since it exhibits a <sup>19</sup>F n.m.r. signal at 136.7 p.p.m., more consistent with a 'tertiary' fluorine atom as contained in structure (3) (=N-CF). 'Tertiary'



fluorine atoms normally give signals at very high field [*e.g.*  $\text{CF}(\text{CF}_3)_2$  in (3) at 186.5 p.p.m.]; the shift to lower field in this case is induced by adjacent nitrogen. Oxygen adjacent to 'tertiary' fluorine has a similar effect.<sup>10</sup>

Ring opening of cyclohexa-1,3-dienes is well known,<sup>11</sup>



giving trienes, and analogous processes involving some heterocyclic systems have also been reported.<sup>12</sup> Clearly, analogous ring opening of (1) to the triene (2) occurs, although this is in contrast to the irradiation of perfluorocyclohexa-1,3-diene (5) where formation of the *para*-bonded species (6) has been observed.<sup>13</sup> Ready ring closure of (2) to (3) is consistent with the known propensity of fluorinated dienes to give corresponding cyclobutenes,<sup>14</sup> *i.e.* the reverse of the position of equilibrium of the corresponding hydrocarbon dienes. The further ready conversion of (3) into (4) could occur by an allylic rearrangement induced by the presence of 'adventitious' fluoride ion, or by a photochemically induced 1,3-shift of fluorine. The latter seems more likely, since the conversion of (3) into (4) occurs so readily and the amounts of fluoride ion available could only be very small indeed.

(11) follows simply from the spectroscopic data, but we are unable to comment on the stereochemistry of the imine groups.

Formation of compounds (8) and (9) from (7) [or from (10)] represents a rare example of a photochemically

induced retro-Diels-Alder reaction. The formation of (11) is also of particular interest, because this ring-opening process must incorporate a 1,3-fluorine shift. We have examined related molecules (12)–(14) but no significant amounts of photoproducts were obtained. The types of retro-Diels-Alder reactions which would apply to (12) and (13) are quite different from those described for (7) and (10). For (14) a comparable retro-Diels-Alder reaction would involve elimination of a fluoro-alkyne, known to be a high-energy species.<sup>15</sup>

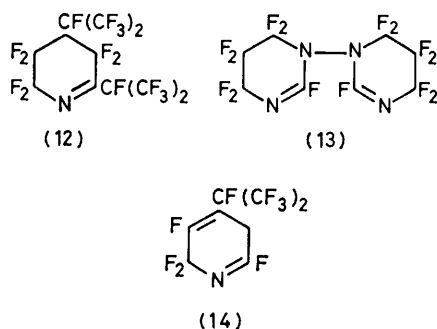
These new examples illustrate the gradually increasing range of skeletal processes that may be studied by use of fluorocarbon systems.

#### EXPERIMENTAL

Spectroscopic data were obtained using the following spectrometers: i.r., Perkin-Elmer 457 or 577; u.v., Pye Unicam SP 800; mass, A.E.I. MS9 or V.G. Micromass 12B linked with g.l.c.; n.m.r., Varian A56/60D or Brüker HX90E. Trichlorofluoromethane was used as external standard and upfield shifts (p.p.m.) are recorded as positive. G.l.c. was carried out using a Varian Aerograph instrument fitted with a gas-density balance detector. Two columns were used: Column O, 30% SE 30 on Chromosorb G60-80; and Column A, 20% di-isodecyl phthalate on Chromosorb P.

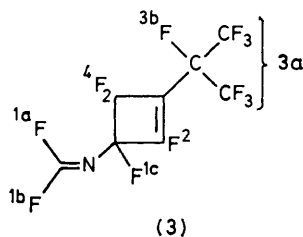
*Irradiations.—General procedure.* All irradiations were carried out using a Rayonet R.P.R. 208 reactor equipped with eight 15 W low-pressure mercury lamps emitting at 253.7 nm. Starting materials were transferred under vacuum into a 34 × 4 cm silica tube, degassed and sealed under high vacuum. After irradiation, products were similarly transferred into a liquid-air-cooled trap attached to an inflatable bladder.

(a) *Perfluoro-4-isopropyl-1-azacyclohexa-1,3-diene* (1). (i) Compound (1) (4.3 g, 12.0 mmol) was irradiated for 72 h. The product (3.9 g) was shown (g.l.c.; Column O at 80 °C) to consist of a mixture of liquids with one major component. Preparative g.l.c. gave *perfluoro-3-methyleneamino-1-iso-*



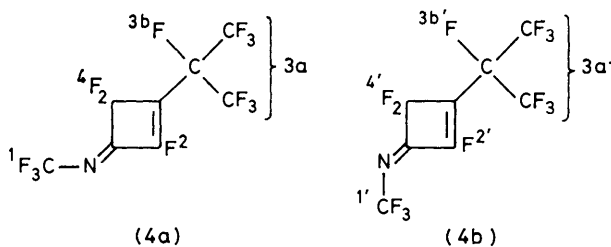
For comparison, the diaza-systems (7) and (10) were irradiated under similar conditions. The derivative (7) was >90% converted into an equimolar mixture of perfluoroisobutyronitrile (8) and a new compound (9) whose structure follows simply from the spectroscopic data. The product mixture (76% conversion) from (10) was more complicated; compounds (8) and (9) were obtained in approximately equimolar amounts, together with the major product (11). The overall structure of

*perfluorocyclobutene* (3) (70%) (Found: C, 27.0; F, 69.3; N, 4.1.  $C_8F_{13}N$  requires C, 26.9; F, 69.2; N, 3.9%);  $M^+$  357;  $\nu_{\max}$  1 680, 1 767, and 1 775  $cm^{-1}$ ;  $\delta_F$  32.9 (1 F, 1a- or 1b-F), 51.2 (1 F, 1a- or 1b-F), 78.2 (m, 6F, 3a-F), 96.1 (1F, 2-F), 114.0 (2F, 4-F), 136.7 [d ( $J$  19 Hz) of t, ( $J$  7.5 Hz) 1F, 1c-F],



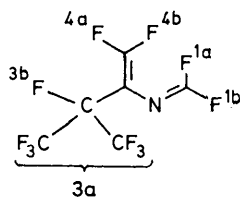
Numbering systems for n.m.r. assignments

and 186.4 (1F, 3b-F). In all subsequent experiments compound (3) could not be obtained in any significant quantity; a different product (4) was obtained. A typical example is as follows: (ii) Compound (1) <sup>7</sup> (3.8 g, 10.6 mmol) was irradiated for 72 h. The product (3.5 g) was shown (g.l.c.; Column O at 80 °C) to consist of one major component. Preparative g.l.c. gave *perfluoro-3-methylimino-1-isopropylcyclobutene* (4) (87%) (Found: C, 27.2; F, 68.7; N, 4.1.  $C_8F_{13}N$  requires C, 26.9; F, 69.2; N, 3.9%);  $M^+$  357;  $\nu_{\max}$  1 682 and 1 765  $cm^{-1}$ . The n.m.r. spectrum indicated a mixture of isomers in the ratio 2 : 1 [(4a) : (4b)]; <sup>19</sup>F signals



were assigned to the two isomers as follows:  $\delta_F$  62.1 (d,  $J$  18 Hz, 1'-F), 62.7 (t,  $J$  8 Hz, 1-F), 79.9 (m, 6F, 3a- and 3a'-F), 80.9 (2'-F), 89.8 (2-F), 104.4 (4-F), 112.2 (4'-F), and 187.7 (1 F, 3b- and 3b'-F).

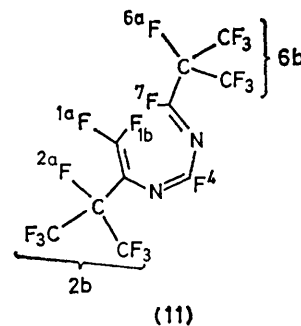
(b) *Perfluoro-2,5-di-isopropyl-1,4-diazacyclohexa-1,4-diene* (7). Compound (7) <sup>7</sup> (3.2 g, 6.5 mmol) was irradiated for 340 h. Products consisted of a gas (1.1 g), identified as perfluoroisobutyronitrile (8) (35%) by comparison of spectroscopic data with those of an authentic sample, and a liquid (1.9 g) shown (g.l.c.; Column A at 60 °C) to consist of a minor amount of (8) and one major component. Preparative g.l.c. gave *perfluoro-3-isopropyl-2-azabuta-1,3-diene* (9) (58%) (Found: C, 24.2; F, 70.5; N, 4.7.  $C_6F_{11}N$  requires C, 24.4; F, 70.8; N, 4.7%);  $M^+$  295;  $\nu_{\max}$  1 732 and 1 805



(9)

$cm^{-1}$ ;  $\delta_F$  42.6 (1F, 1a- or 1b-F), 55.9 (1F, 1a- or 1b-F), 78.9 (6F, 3a-F), 83.1 [d, ( $J$  29 Hz) of t ( $J$  15 Hz) 1F, 4b-F], 93.0 [d ( $J$  59 Hz) of d ( $J$  29 Hz), 1F, 4a-F], and 187.0 (d,  $J$  59 Hz, 1F, 3b-F).

(c) *Perfluoro-4,6-di-isopropyl-1,3-diazacyclohexa-1(6),4-diene* (10). Compound (10) <sup>7</sup> (3.7 g, 7.6 mmol) was irradiated for 140 h. The product (3.5 g) was shown (g.l.c.; Column A at 60 °C) to consist of four components. Preparative g.l.c. gave compounds (8) (11%) and (9) (17%) [identified by comparison of spectroscopic data with samples obtained in (b)], and *perfluoro-7-methyl-2-isopropyl-3,5-diazaocta-1,3,5-triene* (11) (48%) (Found: C, 24.7; F, 69.2; N, 6.2.



$C_{10}F_{18}N_2$  requires C, 24.5; F, 69.8; N, 5.7%);  $\nu_{\max}$  1 678, 1 731, and 1 799  $cm^{-1}$ ;  $\delta_F$  41.8 (2F, 4- and 7-F), 76.6 (6F, 2b- or 6b-F), 77.7 (d,  $J$  26 Hz, 1F, 1b-F), 77.9 (6F, 2b- or 6b-F), 91.3 [d, ( $J$  62 Hz) of d ( $J$  26 Hz), 1F, 1a-F], 182.2 (1F, 6a-F) and 185.9 (d,  $J$  62 Hz, 1F, 3b-F). The fourth component was identified as starting material (10) by comparison of spectroscopic data [yields based on amount of (10) consumed].

Irradiations of compounds (12), (13), and (14) were carried out under similar conditions. On all occasions >95% recovery of starting material was obtained.

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