

Photochemistry of Halogenocarbon Compounds. Part II.^{1,2} Valence Isomers from Fluorinated Pyridazines

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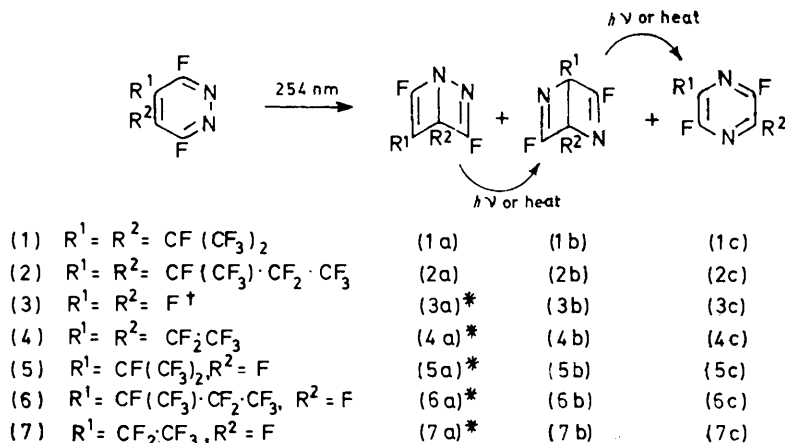
para-Bonded species are obtained by irradiation (at 254 or 300 nm) of perfluoroalkylpyridazines under flow conditions. Perfluoro-1,2-diazabicyclo[2.2.0]hexa-2,5-diene derivatives have been isolated in some cases; these are converted into perfluoro-2,5-diazabicyclo[2.2.0]hexa-2,5-diene derivatives by photo- or thermal reactions or in a process catalysed by firebrick. The *para*-bonded species have also been converted into the corresponding pyrazines; this establishes a new process for 1,3-shifts in an aromatic system. Perfluoro-1,4-diethyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene is remarkably stable to heat, and τ values of this and other valence isomers are discussed.

IN Part I¹ we described some unusual rearrangements of pyridazines to pyrazines and suggested a reaction path which accounted for the specific substituent labelling which was observed. Here we describe experiments designed to isolate intermediates involved in these rearrangements.

The technique used in the photochemical rearrangements described earlier,¹ involved use of sealed tubes and, in some cases, the product mixture contained components other than the pyrazines or starting pyridazine

examined by ¹⁹F n.m.r. The product from derivative (1) contained a mixture of valence isomers (1a and b) along with the pyrazine (1c); the derivative (2) gave the valence isomer (2a), together with the pyrazine (2c).

When compound (1a) was passed through a g.l.c. column, smooth conversion into (1b) occurred, *e.g.* at 28 °C. This was unexpected since (1a) is not converted into (1b) in a sealed tube at this temperature under vacuum or in the presence of air. Furthermore, passing (1a) in a stream of nitrogen over firebrick at 71 °C led to



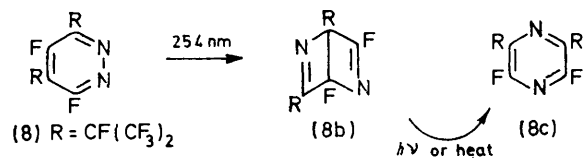
* Not isolated. † Irradiated in a static system.

but only in trace quantities. We reasoned that intermediates were being rearomatised by further photo-reaction and therefore, in subsequent experiments, an apparatus was employed where the products could be removed from the irradiation zone by transference through the zone, under vacuum, to a cold trap. The rate of transference was varied by using a small partial pressure of air, or nitrogen, in the system.

The u.v. spectra of various fluorinated pyridazines have been discussed previously;¹ it is clear that a $\pi-\pi^*$ transition can generally be effected by the emission envelope of a low-pressure mercury lamp (254 nm). A more variable situation obtains with the $n-\pi^*$ transitions but excitation can be effected by using the appropriate light source and filter (300 nm, phosphor; medium-pressure Hg lamp; or 360 nm, phosphor).

Irradiation at 254 nm.—The perfluoro-4,5-dialkylpyridazines (1) and (2) were irradiated and the products were

smooth conversion into (1b), whereas an analogous experiment with glass wool resulted in no conversion. Also, the presence of oxygen appeared to have an inhibiting



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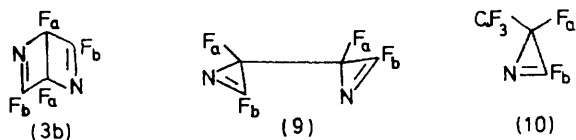
effect on the rearrangement over firebrick. The basis of the catalytic effect of firebrick is not clear at present. Fortunately, however, g.l.c. provided a convenient method of isolating pure samples of (1b) and (2b), from (1a) and (2a), respectively. The valence isomers (3b)—(7b), together with the corresponding pyrazines (3c)—(7c) were isolated after separation of the photoreaction mix-

¹ Part I, R. D. Chambers, J. A. H. MacBride, J. R. Maslakiewicz, and K. C. Srivastava, *J.C.S. Perkin I*, 1975, 396.

² Preliminary communication, R. D. Chambers, W. K. R. Musgrave, and K. C. Srivastava, *Chem. Comm.*, 1971, 264.

tures by g.l.c. Nevertheless, the ^{19}F n.m.r. and i.r. spectra of the photoreaction products before g.l.c. were consistent with the presence of small amounts of (3a)—(7a), although (3b)—(7b) were the major products.

The proportions of products obtained were variable, depending on the partial pressure of air employed (transference time), the size of the apparatus, and the particular pyridazine derivative under investigation; specific examples are given in the Experimental section. As indicated above, the valence isomers (1b)—(8b) were conveniently isolated by g.l.c. since they have significantly shorter retention times than the corresponding pyridazines and pyrazines. Also, vapour pressures of the valence isomers are significantly greater than those of the aromatic compounds and, therefore, are transferred more readily under vacuum. This technique was used for the isolation of (1a) and (2a).



Structures of the *para*-bonded species were determined by i.r. and ^{19}F n.m.r. spectroscopy, *e.g.* resonances at 47.4 and 174.2 p.p.m. (from CFCl_3) were observed for (3b) and the i.r. spectrum showed a strong absorption at 1656 cm^{-1} . A diazabenzvalene structure is ruled out by the presence of only two types of fluorine atom and a diazaprismene structure is also precluded by the i.r. spectrum (showing C=C or C=N stretch). Structure (3b), however, is consistent with these data because it is well established that a 'tertiary' fluorine atom, *i.e.* F_a , gives a characteristically high-field resonance³ whereas a fluorine atom attached to an imine position resonates at much lower field.^{4,5} At first sight, however, a diazabicyclopropenyl structure, *e.g.* (9), which is also a valence isomer of (3), also appears to be consistent with the spectroscopic data. Nevertheless, a comparison of the chemical shift for F_a in compound (10), 98.9 p.p.m. (from CFCl_3 , extrapolated from the value recorded⁶ for $\text{CF}_3\text{-CO}_2\text{H}$ as reference) argues against an azacyclopropene structure (9). Furthermore, the C=N stretching absorption for compound (10) occurs at 1842 cm^{-1} , which is substantially different from the value of 1656 cm^{-1} attributed to (3b). The *para*-bonded species (1b)—(7b) all showed strong C=N stretching absorption in the region $1660\text{--}1690\text{ cm}^{-1}$ and the ^{19}F n.m.r. spectra correspond with the assigned structures (see Experimental section). Furthermore, each of these *para*-bonded species (1b)—(7b) was converted into the corresponding pyrazine (1c)—(7c), as indicated, by heating in a sealed tube or by irradiation.

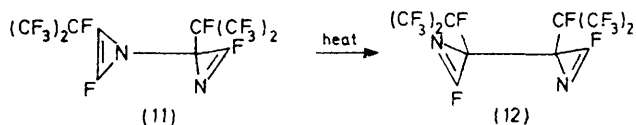
Both (1a) and (2a) showed i.r. bands attributable to C=C and C=N stretching at *ca.* 1735 and 1670 cm^{-1} ,

³ R. D. Chambers, R. P. Corbally, W. K. R. Musgrave, J. A. Jackson, and R. S. Matthews, *J.C.S. Perkin I*, 1972, 1286 and references contained therein.

⁴ R. E. Banks, 'Fluorocarbons and Their Derivatives', MacDonald, London, 1970, p. 237.

⁵ R. D. Chambers, D. T. Clark, T. F. Holmes, W. K. R. Musgrave, and I. Ritchie, *J.C.S. Perkin I*, 1974, 114.

respectively. The ^{19}F n.m.r. spectra contained peaks at low field corresponding to non-equivalent fluorine atoms, *e.g.* at 61.1 and 63.0 p.p.m. for (1a), again substantially different from the value for F_b in (10). Nevertheless, at first sight, these data could be accommodated by a diazabicyclopropenyl structure (11). However, structure (11)



is particularly unlikely since one of the rings is anti-aromatic, *i.e.* a Δ^2 -azirine,⁷ and therefore we can now be confident in excluding not only (11) but also (12) from consideration as an alternative to (1b).

Irradiation of perfluoro-3,5-di-isopropylpyridazine (8) gave a valence isomer (8b) the pyrazine (8c), and minor products which will be discussed in a later publication. The ^{19}F n.m.r. spectrum of (8b) clearly showed a 'tertiary fluorine' signal at high field and a -CF=N- signal at low field, and (8b) was converted thermally or by irradiation into (8c).

Irradiation at 300 nm.—The photoreactions described above clearly involve $\pi\text{-}\pi^*$ transitions and in two cases, (5) and (8), the absorption spectra of the pyridazines are such that, by using a Pyrex filter and irradiating at 300 nm, it was possible to exclude $\pi\text{-}\pi^*$ transitions. In both these cases, the products were the same as those obtained by irradiation at 254 nm; therefore we can assume that absorption of energy by either $\pi\text{-}\pi^*$ or $n\text{-}\pi^*$ transition can lead to rearrangement.

Irradiation of the pyridazines (5) and (6) in Pyrex and at 300 nm gave a mixture containing essentially the starting pyridazine and the valence isomer (5b) or (6b), respectively but no pyrazine derivatives, in contrast to irradiation at 254 nm. After transferring three times the product contained >90% of these valence isomers, with good recovery of material. At 254 nm the *para*-bonded species (5b) and (6b) are probably generated with sufficient internal energy to allow spontaneous conversion into the corresponding pyrazines (5c) and (6c), but in any case (5b) and (6b) are converted into the corresponding pyrazines by irradiation at 254 nm, whereas they are stable to 300 nm radiation in Pyrex.

We have now isolated and identified each stage in a new and remarkable aromatic rearrangement process, which we suggested earlier, but only on the basis of substituent labelling experiments. Furthermore, the rearrangements of isomers (1a) and (2a) to (1b) and (2b), respectively, both photochemically and thermally, are rare examples of conversions of one valence isomer into another of the same type. Indeed it is the only example of which we are aware of such a thermal process; the only similar transformation which we have found involves the photolytic rearrangement of a tri-*t*-butylbenzvalene.^{8,9}

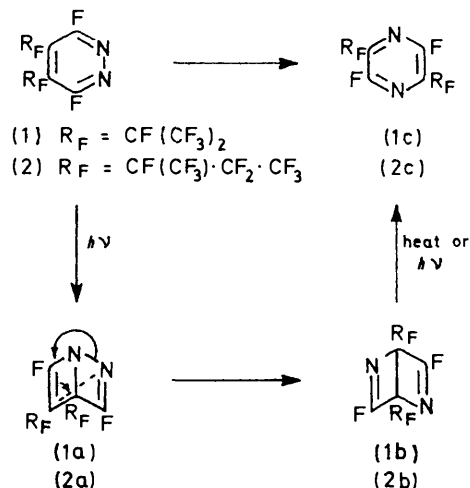
⁸ R. E. Banks and G. J. Moore, *J. Chem. Soc. (C)*, 1966, 2304.

⁹ F. W. Fowler, *Adv. Heterocyclic Chem.*, 1971, 13, 45.

⁸ I. E. Den Besten, L. Kaplan, and K. E. Wiltzbach, *J. Amer. Chem. Soc.*, 1968, 90, 5868.

⁹ I. T. Scott and M. Jones, *Chem. Rev.*, 1972, 72, 181.

The most obvious effect contributing to the driving force for the rearrangement of the (a) series valence isomers to the (b) series, is the removal of a relatively weak N-N bond, but it is also possible that examples of this type of rearrangement will be found in systems other



than pyridazines. Indeed, since such a process would lead to 1,3-shifts, in aromatic systems, it should now be considered as a possible alternative to schemes involving the intermediacy of prismane derivatives, when specific 1,3-shifts are observed.

Properties of the Valence Isomers.—All the *para*-bonded species described above showed strong u.v. absorption between *ca.* 200 and 260 nm; weaker absorption was observed in some cases at much longer wavelength. This is consistent with reports on valence isomers of other aromatic systems^{10,11} but u.v. absorption is a point which is not often emphasised. The absorption accounts for the ready rearomatization by irradiation at 254 nm.

The compounds shown in the Scheme are the first valence isomers of aromatic diazines to be reported, although *para*-bonded isomers of pyridine¹² and fluoro-pyridines¹³ have been described. Some of the diaza-bicyclo[2.2.0]hexadienes reported here are remarkably stable to heat. Valence isomers of benzene¹⁴ and hexafluorobenzene¹⁵ are known to rearomatise, sometimes with explosive violence, whereas with these diaza-derivatives no vigorous rearomatization has been observed, so far. Indeed the perfluoro-diethyl derivative (4b) was not noticeably changed after 45 min at 100 °C and a sample has been stored, unchanged, for 2 years at room temperature. The stabilising influence of perfluoroalkyl groups on valence isomers was first established by other workers,^{11,16,17} with reference to benzene derivatives and, in these cases, not only the *para*-bonded isomers but also benzvalene and prismane derivatives

¹⁰ W. Schäfer, R. Criegee, R. Askani, and H. Grüner, *Angew. Chem. Internat. Edn.*, 1967, **6**, 78.

¹¹ M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc. (C)*, 1970, 1232.

¹² K. E. Wiltzsch and D. J. Rausch, *J. Amer. Chem. Soc.*, 1970, **92**, 2178.

¹³ M. G. Barlow, R. N. Haszeldine, and J. G. Dingwall, *J.C.S. Perkin I*, 1973, 1542.

were isolated. Furthermore, very stable *para*-bonded and aza-prismane isomers of perfluoropentaethylpyridine have been isolated.¹³

Measured half-lives for rearrangement of valence isomers are shown in the Table. There is little significant difference in stability between (1a) and (2a) but major

Thermal stabilities of valence isomers
 ($t_{1/2}$ is the half-life at the temperature indicated)

	$t_{1/2}$	$T/^\circ\text{C}$
(1a) \longrightarrow (1b)	2.4 h	102
(2a) \longrightarrow (2b)	3.6 h	100
(1b) \longrightarrow (1c)	9 h	60
(2b) \longrightarrow (2c)	<i>ca.</i> 5 min	100
(1b) \longrightarrow (1c)	3 h	60
(2b) \longrightarrow (2c)	<i>ca.</i> 4 min	100
(4b) \longrightarrow (4c)	unchanged after 11 h	60
(4b) \longrightarrow (4c)	unchanged after 45 min	100
(8b) \longrightarrow (8c)	1 h	60
(5b) \longrightarrow (5c)	80 min	105
(6b) \longrightarrow (6c)	78 min	100
(7b) \longrightarrow (7c)	143 min	100

differences in stability are apparent between the other valence isomers shown. The reasons for these differences are not clear, *e.g.* why the pentafluoroethyl derivative (4b) is dramatically more stable than any of the others. A decrease in stability occurs in the (b) series with the substituents: $CF_2CF_3 \gg CF(CF_3)_2 > CF(CF_3) \cdot CF_2 \cdot CF_3$, so that a crowding effect is probably involved, but it is also conceivable that there is a special stabilising influence by fluorocarbon groups on small rings, which falls off in the series: $CF_3 > CF_2 \cdot CF_3 > CF(CF_3)_2 \sim CF(CF_3) \cdot CF_2 \cdot CF_3 > C(CF_3)_3$. Other workers¹¹ have shown that CF_3 derivatives of valence isomers of benzene are more stable than the pentafluoroethyl derivatives, and our work shows the large difference between $CF_2 \cdot CF_3$ and $CF(CF_3)_2$ which seems unlikely to be due wholly to steric effects. In other areas^{18,19} there is evidence that C-F bonds adjacent to small rings, *i.e.* F-C-(ring), have an unusually large stabilising influence and it remains to be seen whether other evidence can be obtained to test this developing idea.

EXPERIMENTAL

All reactions described were carried out using a Raymont R.P.R.-208 reactor (Southern New England Ultraviolet Company). The temperature within the irradiation zone, when lamps emitting at 253.7 or 300 nm were employed, was *ca.* 40 °C. Two silica vessels were employed: A (81 × 340 mm) and B (110 × 370 mm). Only one Pyrex vessel (87 × 420 mm) was employed. ¹⁹F N.m.r. spectra were recorded on a Varian A56/60D spectrometer; all shifts are quoted relative to $CFCl_3$ (as external reference) (upfield shifts are quoted as positive).

¹⁴ W. Schäfer and H. Hellmann, *Angew. Chem. Internat. Edn.*, 1967, **5**, 518, and references contained therein.

¹⁵ G. Camaggi and F. Gozzo, *J. Chem. Soc. (C)*, 1969, 489.

¹⁶ D. M. Lemal, J. V. Staros, and V. Austel, *J. Amer. Chem. Soc.*, 1969, **91**, 3373.

¹⁷ D. M. Lemal and L. H. Dunlap, *J. Amer. Chem. Soc.*, 1972, **94**, 6562.

¹⁸ R. Hoffmann, *Tetrahedron Letters*, 1970, 2907.

¹⁹ C. W. Jefford, U. Berger, W. Broeckx, and J. C. E. Gehret, *Tetrahedron Letters*, 1973, 2483.

Irradiations at 253.7 nm

One transference experiment is described in detail; subsequent experiments were carried out in an identical manner except where stated otherwise.

Perfluoro-4,5-di-isopropylpyridazine (1).—Perfluoro-4,5-di-isopropylpyridazine²⁰ (1) (9.5 g) was introduced into the silica vessel (A), which was connected to a cold trap. The system was then evacuated to 0.1 mmHg and irradiated, while the substrate (1) distilled towards the cold trap (liquid air), for 119 h. The transferred material (6.7 g) was found by g.l.c. to contain three components (28, 22, and 50%, in order of increasing retention time).

(a) *Isolation of perfluoro-1,4-di-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene* (1b). Preparative scale g.l.c. at room temperature gave *perfluoro-1,4-di-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene* (1b) (1.3 g) (Found: C, 26.7; F, 67.5%; M^+ , 452. $C_{10}F_{16}N_2$ requires C, 26.55; F, 67.25%); ν_{\max} 1678s cm^{-1} (C=N str.); ^{19}F δ 37.1 (3- and 6-F), 75.0 [1- and 4-(CF_3)-CF], and 181.1 p.p.m. [1- and 4-(CF_3)₂CF]. Perfluoro-2,5-diisopropylpyrazine (1c) (0.6 g), identified by comparison of its i.r. and n.m.r. spectra with those of an authentic sample,²¹ and starting material (1) (1.1 g) were also isolated.

(b) *Isolation of perfluoro-4,5-di-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene* (1a). Distillation of a reaction mixture very similar to that above, obtained by transference without g.l.c., at reduced pressure (5.0 mmHg), gave *perfluoro-4,5-di-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene* (1a) (ca. 1.2 g) (Found: F, 67.3%; M^+ , 452. $C_{10}F_{16}N_2$ requires F, 67.25%); ν_{\max} 1735s (C=C str.) and 1670 cm^{-1} (C=N str.); ^{19}F δ 61.1 (3-F), 63.0 (6-F), 76.4 [4-(CF_3)₂CF], 80.1 [5-(CF_3)₂-CF], 181.1 [4- and 5-(CF_3)₂CF]; λ_{\max} 225 nm (ϵ ca. 1750).

Perfluoro-4,5-di-s-butylpyridazine (2).—Perfluoro-4,5-di-s-butylpyridazine²² (2) (5.0 g) was irradiated in vessel A during transference (0.5 mmHg) to the cold trap. After 70 h g.l.c. of the material (2.6 g) which had been transferred showed three major components (25, 35, and 30%, in order of increasing retention time).

(a) *Isolation of perfluoro-1,4-di-s-butyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene* (2b). Preparative scale g.l.c. at 25 °C gave *perfluoro-1,4-di-s-butyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene* (2b) (0.50 g), M^+ 552. Further characterisation was achieved by conversion into the pyrazine derivative (2c) (by heating at 150 °C), which was identified by comparison of spectra with those of an authentic specimen. The valence isomer (2b) showed λ_{\max} 1677s cm^{-1} (C=N str.); ^{19}F δ 36.6 (3- and 6-F), 74.2 [1- and 4- $CF_3CF_2(CF_3)CF$], 82.4 [1- and 4- $CF_3CF_2(CF_3)CF$], 122.2 [$CF_3CF_2(CF_3)CF$], and 187.8 p.p.m. [1- and 4- $CF_3CF_2(CF_3)CF$]. Perfluoro-2,5-di-s-butylpyrazine (2c) (0.65 g) and starting material (2) (0.4 g) were also isolated.

(b) *Isolation of perfluoro-4,5-di-s-butyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene* (2a). Distillation of a similar reaction mixture, obtained by transference without g.l.c., at 4.5 mmHg, gave *perfluoro-4,5-di-s-butyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene* (2a) (ca. 0.40 g) (Found C, 26.4; F, 68.5%; M^+ , 552. $C_{12}F_{20}N_2$ requires C, 26.1; F, 68.8%); λ_{\max} 1735s (C=C str.) and 1669s cm^{-1} (C=N str.); ^{19}F δ 62.2 (3-F), 62.6 (6-F), 74.5 [4- $CF_3CF_2(CF_3)CF$], 77.8 [5- $CF_3CF_2(CF_3)CF$], 82.8 [4- and 5- $CF_3CF_2(CF_3)CF$], 117.7 [4- $CF_3CF_2(CF_3)CF$], 123.4 [5- $CF_3CF_2(CF_3)CF$], 176.4 [4- $CF_3CF_2(CF_3)CF$], and 186.6 p.p.m. [5- $CF_3CF_2(CF_3)CF$]; λ_{\max} 223 nm (ϵ ca. 1590).

²⁰ R. D. Chambers, Yu. A. Cheburkov, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1971, 532.

²¹ R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1971, 3384.

Tetrafluoropyridazine (3).—Tetrafluoropyridazine (3) (5.0 g) was sealed in a silica tube and irradiated for 65 h. The crude product was found by g.l.c. and ^{19}F n.m.r. spectroscopy to contain three major components (10, 33, and 55% in order of increasing g.l.c. retention time). Preparative scale g.l.c. gave *perfluoro-2,5-diazabicyclo[2.2.0]hexa-2,5-diene* (3b) (0.2 g), M^+ 152. Further characterisation was achieved by conversion into the pyrazine (3c), after heating at 150 °C in a sealed ampoule, which was identified by comparison of spectra with those of an authentic specimen.²³ The valence isomer (3b) showed λ_{\max} 1656s cm^{-1} (C=N str.); ^{19}F δ 47.4 (3- and 6-F) and 172.2 p.p.m. (1- and 4-F). Tetrafluoropyrazine (3c) and tetrafluoropyridazine (3) were also isolated.

Perfluoro-4,5-diethylpyridazine (4).—Perfluoro-4,5-diethylpyridazine (4) (1.65 g) was irradiated in vessel A during transference (0.001 mmHg) to the cold trap. The product was re-irradiated under the same conditions. G.l.c. of the final product (1.58 g) showed three major components, and preparative scale g.l.c. gave *perfluoro-1,4-diethyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene* (4b) (0.33 g) (Found: F, 65.3%; M^+ , 352. $C_8F_{12}N_2$ requires F, 64.75%); λ_{\max} 1672s cm^{-1} (C=N str.); ^{19}F δ 38.6 (3- and 6-F), 84.9 (1- and 4- CF_3CF_2), 121.2 [1- and 4- $CF_3(F)CF$], and 125.8 p.p.m. [1- and 4- $CF_3(F)CF$] (*N.B.* the latter two shifts were calculated from the second-order spectrum). Perfluoro-2,5-diethylpyrazine (4c) (0.45 g) and starting material (4) (0.6 g) were also isolated.

Perfluoro-3,5-di-isopropylpyridazine (8).—Perfluoro-3,5-di-isopropylpyridazine (8) (8.2 g) was irradiated in vessel A during transference (0.001 mmHg) to the cold trap. After 18 h the reaction was stopped and the product (7.5 g), analysed by g.l.c., showed three major components. Preparative scale g.l.c. gave *perfluoro-1,3-di-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene* (8b) (1.2 g) (Found: C, 26.8; F, 67.0%; M^+ , 452. $C_{10}F_{16}N_2$ requires C, 26.55; F, 67.25%); λ_{\max} 1688s cm^{-1} (C=N str.); ^{19}F δ 42.2 (6-F), 75.0 [1- $CF_3(CF_3)CF$], 76.2 [1- $CF_3(CF_3)CF$], 3-(CF_3)₂CF], 162.1 (4-F), 187.1 [1-(CF_3)₂CF], and 192.0 [3-(CF_3)₂CF]. Perfluoro-2,6-di-isopropylpyrazine (8c) (0.15 g) and starting material (8) (3.5 g) were also isolated.

Perfluoro-4-isopropylpyridazine (5).—Perfluoro-4-isopropylpyridazine (5) (5.0 g) was irradiated in vessel A during transference (2.0 mmHg) to the cold trap. The product was re-irradiated during transference (3.0 mmHg) and the final product (4.9 g) was found by g.l.c. to contain three major components. Preparative g.l.c. gave *perfluoro-2,5-diaza-1-isopropylbicyclo[2.2.0]hexa-2,5-diene* (5b) (1.8 g), M^+ 302. Further characterisation was achieved by conversion into the pyrazine (5c),¹ on heating in a sealed tube at 150°. The valence isomer (5b) showed λ_{\max} 1665s cm^{-1} (C=N str.); ^{19}F δ 42.4 (6-F), 45.0 (3-F), 75.9 [1- $CF_3(CF_3)CF$], 77.1 [1- $CF_3(CF_3)CF$], 166.6 (4-F), and 187.7 p.p.m. [(CF_3)₂CF]. Perfluoro-2-isopropylpyrazine (5c) (2.2 g) and starting material (0.10 g) were also isolated.

Perfluoro-4-s-butylpyridazine (6).—Perfluoro-4-s-butylpyridazine (6) (1.8 g) was irradiated in vessel A during transference (0.5 mmHg) to the cold trap. The product (1.7 g) was found by g.l.c. to contain three major components. Preparative scale g.l.c. gave *perfluoro-2,5-diaza-1-s-butylbicyclo[2.2.0]hexa-2,5-diene* (6b) (0.20 g), M^+ 352. Further

²² R. D. Chambers, J. A. Jackson, P. D. Philpot, and A. C. Young, *J. Fluorine Chem.*, in the press.

²³ C. G. Allison, R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1970, 1023.

characterisation was achieved by conversion into the pyrazine (6c),¹ on heating in a sealed tube at 150 °C. Compound (6b) showed λ_{\max} 1661s cm⁻¹ (C=N str.); ¹⁹F δ 42.1 (6-F), 45.5 (3-F), 74.5 [CF₃CF₂(CF₃)·CF], 83.0 [CF₃CF₂(CF₃)·CF], 119.2 (CF₃CF₂(CF₃)·CF), 165.6 (4-F), and 185.1 p.p.m. [CF₃CF₂(CF₃)·CF]. Perfluoro-2-s-butylpyrazine (6c) (0.75 g) and starting material (6) (0.3 g) were also isolated.

Perfluoro-4-ethylpyridazine (7).—Perfluoro-4-ethylpyridazine (7) (1.8 g) was irradiated in vessel B during transference (5 mmHg) to the cold trap. The product (1.7 g) was found by g.l.c. to contain three major components. Preparative scale g.l.c. gave *perfluoro-1-ethyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene* (7b) (0.20 g) (Found: F, 59.7%; *M*⁺, 252. C₆F₈N₂ requires F, 60.3%); λ_{\max} 1660s cm⁻¹ (C=N str.); ¹⁹F δ 43.9 (6-F), 44.8 (3-F), 86.2 [1-CF₃(F)CF], 124.7 [1-CF₃(F)CF], 127.3 [1-CF₃(F)CF] (methylene fluorine shifts calculated due to second order spectrum), and 163.9 p.p.m. (4-F). Perfluoroethylpyrazine (7c) (0.7 g) and starting material (7) (0.31 g) were also isolated.

Irradiations at 300 nm

Perfluoro-4-isopropylpyridazine (5).—Perfluoro-4-isopropylpyridazine (5) (8.45 g) was irradiated in a Pyrex vessel during transference (4 mmHg) to the cold trap, and then the product was twice re-irradiated under approximately the same conditions. The final product was found by ¹⁹F n.m.r. and g.l.c. to be a mixture of perfluoro-2,5-diaza-1-isopropylbicyclo[2.2.0]hexa-2,5-diene (5b) (94%), perfluoro-2-isopropylpyrazine (5c) (1%), and starting material (5) (5%).

Perfluoro-4-s-butylpyridazine (6).—Perfluoro-4-s-butylpyridazine (5) (1.5 g) was irradiated in Pyrex during transference (0.5 mmHg) to the cold trap. The product was then re-irradiated under approximately the same conditions a further three times. The final product was found by g.l.c. and ¹⁹F n.m.r. to contain perfluoro-1-s-butyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (6b) (57%), perfluoro-2-s-butylpyrazine (6c) (trace), and starting material (6).

Irradiation of Perfluoro-4,5-di-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (1a).—Perfluoro-4,5-di-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (1a) (100 mg) was sealed under high vacuum in a dry silica tube (4 × 120 mm), and irradiated at 253.7 nm for 19 h. ¹⁹F N.m.r. spectroscopy showed the product to be a mixture of starting material (1a), perfluoro-1,4-di-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene (1b), and perfluoro-2,5-di-isopropylpyrazine (1c) in the ratio *ca.* 1 : 1 : 1.

Rearrangement of Perfluoro-4,5-di-isopropyl-1,2-diazabicyclo[2.2.0]hexa-2,5-diene (1a) to *Perfluoro-1,4-di-isopropyl-2,5-diazabicyclo[2.2.0]hexa-2,5-diene* (1b).—The 1,2-diazabicyclohexadiene (1a) (0.30 g) was passed through a tube packed with firebrick (80–100 mesh) (14 × 160 mm) at 71 °C in a stream of nitrogen (contact time *ca.* 4–5 min). The product (0.25 g) was found by g.l.c. and ¹⁹F n.m.r. and i.r. spectroscopy to be a mixture of starting material (1a) (26%), the 2,5-diazabicyclohexadiene (1b) (68%), and perfluoro-2,5-di-isopropylpyrazine (1c) (6%).

In an identical experiment where oxygen was the carrier gas the product was a mixture of starting material (1a) (88%), the 2,5-diazabicyclohexadiene (1b) (10%), and perfluoro-2,5-di-isopropylpyrazine (1c) (2%).

Passing (1a) (0.20 g) through a tube (14 × 350 mm), at 76 °C, loosely packed with glass wool in a stream of nitrogen (contact time *ca.* 7 min) gave only unchanged starting material (1a).

Thermal Stability of the Perfluorodiazabicyclohexadienes Isolated.—The individual isomers were either sealed in n.m.r. tubes with hexafluorobenzene (as standard) and heated in the probe, or heated in sealed tubes and examined periodically by g.l.c. (gas density balance). The isomers rearranged with first-order kinetics. The half-lives are given in the Table.

We thank the S.R.C. for financial assistance.

[4/2273 Received, 4th November, 1974]