Photochemistry of Halogenocarbon Compounds. Part 3.[1,2] Rearrangements involving Azaprismanes

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Irradiation of perfluoroalkylpyridines containing a high degree of substituent labelling gives in each case a 1-azabicyclo[2.2.0]hexadiene derivative and azaprismanes, which exhibit high thermal stability. Structures of the azaprismanes have been deduced by rearomatisation to pyridines, which are characterised by their ^{19}F n.m.r. spectra; the spectra reveal conformational preferences for perfluoro-isopropyl and -ethyl groups. To account for the structures of the azaprismanes obtained, rearrangement of an initially produced 2-azabicyclo[2.2.0]hexadiene derivative to the 1-aza-isomer is suggested.

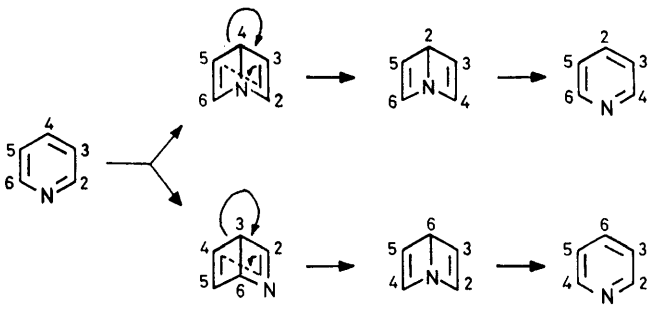
In previous work on fluorinated pyridazines, we have established a novel mechanism for a 1,3-shift, involving the intermediacy of *para*-bonded species.[1] We now report work designed to reveal any analogous process in the pyridine system. This is illustrated in Scheme 1, where two examples of the various possible 1,3-shifts are illustrated; these would be P_8 types, in terms of the notation recently introduced by Barltrop and Day.[3]

We have been using fluoro and perfluoroalkyl groups effectively as 'passive' substituents,[1,4,5] in order to detect skeletal rearrangements; obviously, a high degree of substituent labelling is required in order to detect the types of shift illustrated in Scheme 1. The pyridine derivatives (1) and (2), synthesised previously in these laboratories,[6] are ideal for the purpose, *e.g.* (1) contains four different labels, if the ring nitrogen is included.

Irradiation of (1) (in $CF_2Cl{\cdot}CFCl_2$) at 254 nm gave mixtures containing the *para*-bonded species (3) and two azaprismanes (4) and (5). That the *para*-bonded species has the symmetrical structure (3) follows from the ^{19}F n.m.r. and i.r. spectra, which showed *e.g.* only one resonance arising from CF_3 attached to the ring, and a C=C stretching band at 1 692 cm^{-1}. Heating the *para*-bonded species (3) gave the starting pyridine derivative (1). The azaprismane structures follow from u.v. and i.r. data, in comparison with data for (1) and (3); ^{19}F n.m.r. spectra indicate symmetrical and unsymmetrical structures for (4) and (5) respectively. These observations parallel those made earlier with perfluoropentaethylpyridine, which gives a *para*-bonded isomer and a remarkably stable azaprismane on irradiation.[7] Similarly, the azaprismanes (4) and (5) have a

[1] Part 2, R. D. Chambers, J. R. Maslakiewicz, and K. C. Srivastava, *J.C.S. Perkin I*, 1975, 1130.
[2] Preliminary communication, R. D. Chambers, R. Middleton, and R. P. Corbally, *J.C.S. Chem. Comm.*, 1975, 731.
[3] J. A. Barltrop and A. C. Day, *J.C.S. Chem. Comm.*, 1975, 177.
[4] R. D. Chambers, J. A. H. MacBride, J. Maslakiewicz, and K. C. Srivastava, *J.C.S. Perkin I*, 1975, 396.
[5] R. D. Chambers, M. Clark, J. R. Maslakiewicz, W. K. R. Musgrave, and P. Urben, *J.C.S. Perkin I*, 1974, 1513.
[6] R. D. Chambers, R. P. Corbally, T. F. Holmes, and W. K. R. Musgrave, *J.C.S. Perkin I*, 1974, 108.
[7] M. G. Barlow, R. N. Haszeldine, and J. G. Dingwall, *J.C.S. Perkin I*, 1973, 1542.

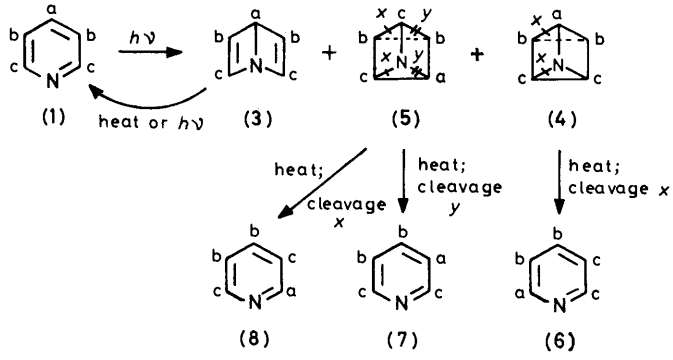
high degree of thermal stability, and were only slowly converted, at 175 °C, into the pyridines (6)—(8), which were separated by g.l.c. The azaprismanes (4) and (5) together gave a single peak on various column packings, but mixtures of various compositions were obtained by fractional distillation; consequently, by pyrolysis of



SCHEME 1

these mixtures we were able to deduce that the symmetrical azaprismane (4) gave a single pyridine derivative (6), whereas the unsymmetrical azaprismane (5) gave a mixture of pyridine derivatives (7) and (8).

To deduce the structures of the isomeric pyridines (6)—(8) from their ^{19}F n.m.r. spectra at first sight appears to be a complex problem, but it is made relatively straightforward by the fact that $CF(CF_3)_2$ groups which are adjacent to ring nitrogen adopt the average conformations shown in, for example, structure

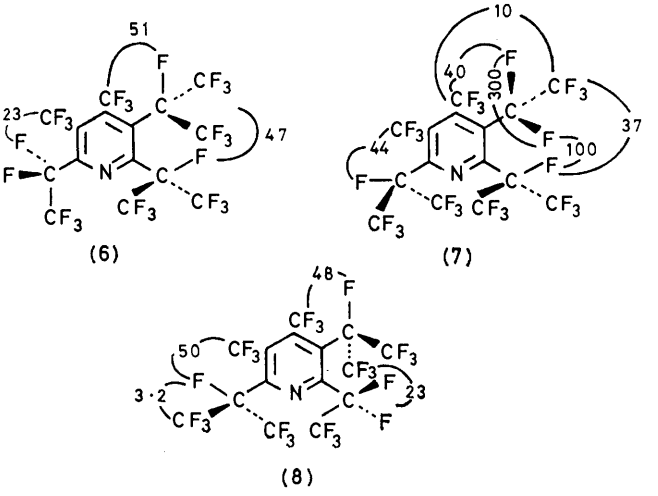


a = CF_2CF_3; b = CF_3; c = $CF(CF_3)_2$

SCHEME 2

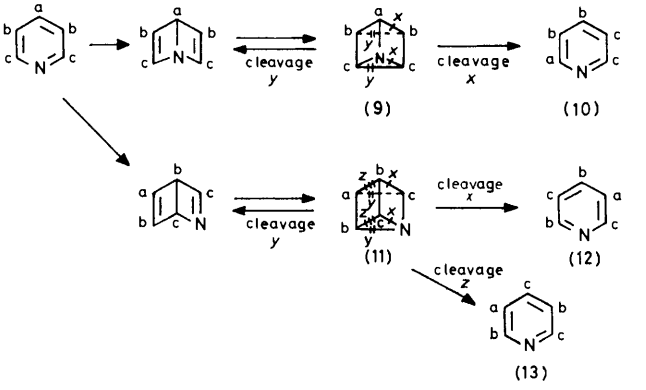
(6) in Scheme 3, with the CF_3 groups flanking the ring nitrogen.[6,8] Consequently, $CF(CF_3)_2$ groups in this environment are readily identified because they show relatively sharp CF_3 signals. A pentafluoroethyl group adjacent to ring nitrogen adopts a similar conformation and can be correspondingly easily identified. With $CF(CF_3)_2$ and C_2F_5 established as adjacent to nitrogen in (6), it is then clear from coupling constants that $CF(CF_3)_2$ groups are adjacent in the ring, and the C_2F_5 is adjacent to CF_3. Also, CF_3 and $CF(CF_3)_2$ are shown to be adjacent, and these deductions firmly establish the structure (6). Similar arguments lead to the assignments of structures (7) and (8). The spectrum of (7) reveals the additional interesting feature of C_2F_5 in a locked conformation between $CF(CF_3)_2$ and CF_3, and the non-equivalence of the geminal fluorine atoms in C_2F_5 is clear from the observation of an AB system (J_{AB} *ca.* 300 Hz). A similar feature has been detected in perfluoropentaethylpyridine.[7] Fuller description of the ^{19}F n.m.r. data is given in the Experimental section.

It is useful at this point to consider the possible isomer patterns that could, in principle, be obtained by formation of azaprismanes from a pyridine derivative



SCHEME 3 *J* Values (Hz)

containing the same degree of substituent labelling as (1), followed by rearomatisation. The various possibilities are shown in Scheme 4, and the main conclusion is that a symmetrical azaprismane (9) could lead to a



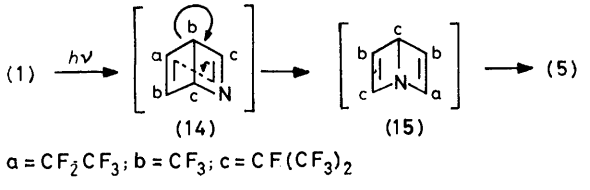
SCHEME 4

single new pyridine derivative (10) whereas the unsymmetrical azaprismane (11) could lead to two new pyridine derivatives (12) and (13), in addition to reforming the starting pyridine derivative in each case.

[8] R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, 1970, **26**, 71.

Indeed van Bergen and Kellogg [9] irradiated a derivative containing this pattern (a = Pr^i; b = CO_2Et; c = Me) and isolated derivatives with structures corresponding to (10), (12), and (13). Although no intermediate azaprismanes or *para*-bonded species were detected, it seems likely that the process outlined in Scheme 4 had taken place.

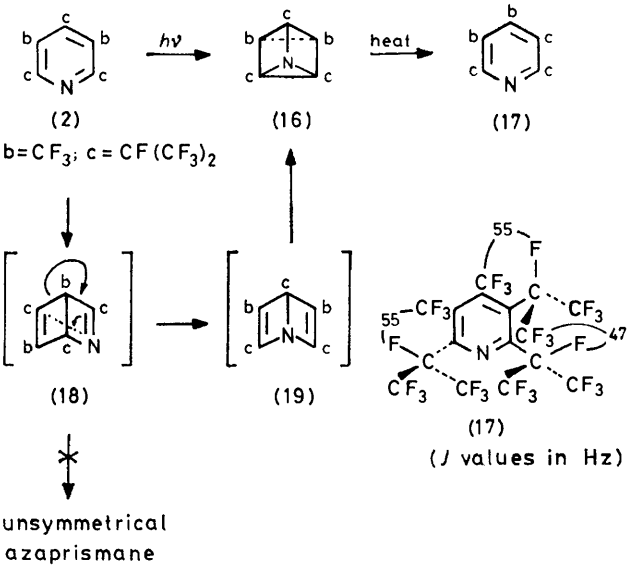
Comparison of the structures of products (6)—(8) with the theoretical system in Scheme 4 shows that the pattern of (6) from the symmetrical azaprismane (4) agrees with the theoretical pattern (10). No starting material (1) was re-formed, but this is probably a result of the easier cleavage of C–N than of C–C. There is no agreement, however, in comparing the patterns of (7) and (8) with the theoretical patterns (12) and (13), from the unsymmetrical azaprismanes. The pyridine derivatives (7) and (8) can only arise from structure (5) for the unsymmetrical azaprismane, and therefore the divergence from the theoretical pattern stems from the different structures (5) and (11) for the intermediate unsymmetrical azaprismanes. We thus have the problem of accounting for the formation of (5) from (1), and this is where the rearrangement outlined in Scheme 1 seems to come in. We suggest that structure (5) is produced by the initial formation of the 2-azabicyclo-[2.2.0]hexadiene derivative (14), followed by immediate rearrangement to the 1-azabicyclo[2.2.0]hexadiene derivative (15) and then cyclisation. The driving force appears to be the relief of steric strain: structure (14) contains four bulky perfluoroalkyl groups in a cyclobutene ring, whereas (15) contains only three. It is important that in both this and earlier work [7] only the 1-azabicyclo-[2.2.0]hexadiene isomers of perfluoropenta-alkylpyridines have been isolated, although simple bond energy summations for the ring indicate that the 2-aza-isomer is the preferred form for the skeleton. Indeed, it has



SCHEME 5

been shown that the *para*-bonded isomer of pyridine has the 2-azabicyclo[2.2.0]hexadiene structure [10] and it is clear, therefore, that the perfluoroalkyl groups have a dominant affect. Alternative mechanisms are possible for producing (5), involving rearrangement of the *para*-bonded isomer (3) by a process illustrated in Scheme 1. However, further irradiation of the *para*-bonded isomer (3) gave mainly the starting material (1), and it is probable that the small amounts of azaprismane derivatives (4) and (5) in the mixture were produced directly from (1), rather than from (3). Also, there is a more obvious driving force apparent for the rearrangement of (14) to (15) and, furthermore, the results of irradiation of perfluorotri-isopropyl-3,5-dimethylpyridine (2) support this conclusion.

Surprisingly, only one azaprismane, the symmetrical isomer (16), was obtained, which gave the new pyridine derivative (17) on heating. According to Scheme 4, however, an unsymmetrical azaprismane could also be formed from (2). The rearrangement process which we have just suggested to account for the formation of (5), *via* (14) and (15), is, nevertheless, in complete accord with the formation of (16); see Scheme 6. The valence isomer (16) could be produced from (2) *via* direct



SCHEME 6

formation of the 1-azabicyclo[2.2.0]hexadiene derivative (19), but if the 2-aza-isomer (18) is formed, then rearrangement would also produce (19) and hence the same azaprismane derivative (16).

In summary, our results are best accounted for in terms of formation of both 1-aza- and 2-aza-bicyclo-[2.2.0]hexadienes, at least in excited states, from (1) and (2) on irradiation. It appears that whereas the 1-aza-isomer can form an azaprismane derivative directly, the 2-aza-isomer undergoes prior rearrangement to the 1-aza-isomer, in preference to formation of an azaprismane derivative directly. These processes, *i.e.* further rearrangements of *para*-bonded species, most likely occur *via* excited states, but it is not clear whether these are electronically or vibrationally excited.

EXPERIMENTAL

All irradiations were carried out with a Rayonet RPR-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. For small-scale fractional distillations a Büchi, Fischer-Spaltrohr MMS200 column was employed. Isomer ratios

[9] T. J. van Bergen and R. M. Kellogg, *J. Amer. Chem. Soc.*, 1972, **94**, 8451.

[10] K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, 1970, **92**, 2178.

were determined either by ^{19}F n.m.r. spectroscopy or by g.l.c. (gas-density balance detector; equal response assumed for the isomers). ^{19}F N.m.r. spectra were recorded with a Brüker HX90E instrument. All shifts are quoted relative to $CFCl_3$ (as internal reference) and spectra of pyridine derivatives were recorded for solutions in $(CD_3)_2CO$; spectra of azaprismane derivatives, which are generally insoluble in this solvent, were recorded for neat liquids. Spectra of compounds (8) and (17) were recorded with a Varian A56/60D spectrometer ($CFCl_3$ as external reference).

Irradiation Experiments.—(a) *Perfluoro-4-ethyl-2,6-di-isopropyl-3,5-dimethylpyridine* (1) *at* 253.7 nm. The pyridine derivative (1) [6] (1 g, 1.49 mmol) in $CF_2Cl{\cdot}CFCl_2$ (20 ml), contained in a stoppered silica flask (capacity *ca.* 30 ml), was irradiated for 196 h at 253.7 nm (120 W); analysis by g.l.c. (silicone elastomer, 78 °C) showed quantitative conversion into one new component. Removal of solvent by distillation and purification of the residue by preparative scale g.l.c. gave perfluoro-4-ethyl-2,6-di-isopropyl-3,5-dimethyl-1-azatetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (4) and perfluoro-2-ethyl-4,6-di-isopropyl-3,5-dimethyl-1-azatetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (5) as a liquid mixture (*ca.* 50 : 50 by ^{19}F n.m.r.) (Found: F, 71.2%; *M*, 669. Calc. for $C_{15}F_{25}N$: F, 71.0; *M*, 669). That these compounds have an azaprismane structure follows from the u.v. spectrum of the mixture: $\lambda_{max.}$ *ca.* 212 nm (ε 297), which shows that the system is not aromatic, and the i.r. spectrum, which shows no C=C or C=N stretching bands. Fractional distillation of the mixture (10 mmHg) gave a small quantity of a mixture containing (5) and (4) in the ratio 55 : 45 (^{19}F n.m.r.), b.p. 65°. This enabled the ^{19}F n.m.r. data for (4) and (5) to be distinguished: ^{19}F δ (4) 73.4 [2- and 6-CF(CF_3)$_2$], 181.0 [2- and 6-CF(CF$_3$)$_2$], 61.2 (3- and 5-CF$_3$), 82.5 (4-CF_3CF$_2$), and 121.2 p.p.m. (4-CF$_3$CF_2); ^{19}F δ (5), 82.5 (2-CF_3CF$_2$), 114.5 [2-CF$_3$(F)CF], 119.3 [2-CF$_3$(F)CF], 62.0 (3- and 5-CF$_3$), 73.4 [4- and 6-CF(CF_3)$_2$], 186.7 [4-CF(CF$_3$)$_2$], and 183.6 p.p.m. [6-CF(CF$_3$)$_2$].

In a similar experiment, irradiation of a solution of the pyridine derivative (1) in perfluoromethylcyclohexane gave the azaprismanes (4) and (5) in relative proportions identical with those quoted above.

(b) *Irradiation of the pyridine* (1) *at* 253.7 nm *for a shorter time.* The pyridine derivative (1) (4 g, 5.97 mmol), in $CF_2Cl{\cdot}CFCl_2$ (80 ml), contained in a stoppered silica tube (*ca.* 100 ml capacity) was irradiated at 253.7 nm (120 W) for 46 h. Analysis of the product by linked g.l.c. (silicone elastomer 78 °C)–mass spectrometry showed the presence of the *para*-bonded species (3), the azaprismanes (4) and (5), and starting material (1) in the ratio 20 : 15 : 65, respectively. Small samples of (3) and a mixture of (4) and (5) were obtained by reduced pressure fractional distillation (18 mmHg; b.p.s of fractions 69 and 73 °C, respectively), and identified by comparison of their ^{19}F n.m.r. spectra with those of authentic samples (see other experiments).

(c) *Irradiation of the pyridine* (1) *at* 300 nm. The pyridine derivative (1) (1.5 g, 2.24 mmol) in $CF_2Cl{\cdot}CFCl_2$ (25 ml), contained in a Pyrex tube (35 ml), was irradiated at 300 nm (*ca.* 42 W) for 24 h. Solvent was removed by distillation and analysis by g.l.c. showed three components. Products from two identical experiments were combined and distilled (13 mmHg), giving *perfluoro-4-ethyl-2,6-di-isopropyl-3,5-dimethyl-1-azabicyclo*[2.2.0]*hexa-2,5-diene* (3) (1.2 g), b.p. 64 °C (Found: C, 27.0; F, 70.7%; *M*, 669. $C_{15}F_{25}N$ requires C, 26.9; F, 71.0%; *M*, 669), $\nu_{max.}$ 1 692 cm^{-1} (C=C str.); ^{19}F δ 77.0 and 78.6 [2- and 6-CF(CF_3)$_2$; these separate absorptions for CF_3 are of equal intensity and arise from restricted rotation of the perfluoro-isopropyl groups [8]], 188.2 [2- and 6-CF(CF$_3$)$_2$], 64.5 (3- and 5-CF$_3$), 84.4 (4-CF$_2$CF_3), and 118.2 p.p.m. (4-CF_2CF$_3$) [J(4-CF$_2$,3-CF$_3$) = J(4-CF$_2$,5-CF$_3$) = 6 Hz]. Analysis of the distillation residue (1.7 g) by g.l.c. showed the presence of (3) (1.1 g), azaprismanes (4) and (5) (0.3 g), and (1) (0.3 g).

In an analogous experiment, but with irradiation for 359 h, the product was a mixture of azaprismanes (4) and (5) in the ratio 45 : 55, *i.e.* a ratio of isomers which is usefully different from that in experiment (a).

(d) *Irradiation of Perfluoro-2,4,6-tri-isopropyl-3,5-dimethylpyridine* (2) *at* 253.7 nm. The pyridine (2) (1.01 g, 1.40 mmol) in $CF_2Cl{\cdot}CFCl_2$ (20 ml), contained in a silica tube (*ca.* 30 ml) was irradiated at 253.7 nm (*ca.* 60 W) for 396 h. Analysis of the product by g.l.c. showed the presence of the azaprismane (16) and starting material (2) in the ratio 61 : 39. Solvent was removed by distillation and the residue was separated by preparative-scale g.l.c. (silicone elastomer; 95 °C) to give *perfluoro-2,4,6-tri-isopropyl-3,5-dimethyl-1-azatetracyclo*[2.2.0.0^{2,6}.0^{3,5}]*hexane* (16) (Found: F, 71.5%; *M*, 719. $C_{16}F_{27}N$ requires F, 71.35%; *M*, 719). The u.v. spectrum [$\lambda_{max.}$ 214 (ε 520) and *ca.* 256 nm (86)] shows that the system is not aromatic, and the i.r. spectrum shows no absorptions corresponding to C=C or C=N stretching. The ^{19}F n.m.r. spectrum shows δ 76.3 and 76.7 [2-, 4-, and 6-CF(CF_3)$_2$], 182.4 [2- and 6-CF(CF$_3$)$_2$], 189.5 [4-CF(CF$_3$)$_2$], and 64.3 p.p.m. (3- and 5-CF$_3$).

Pyrolysis of Mixtures of Azaprismanes (4) *and* (5).—The pyrolyses were carried out several times to establish that the results are reproducible; a typical experiment is described below.

The mixture of azaprismanes (4) and (5) (*ca.* 50 : 50 by ^{19}F n.m.r.) (2.0 g) was sealed, under vacuum, in a thick-walled Pyrex Carius tube (70 × 10 mm) and then heated in a thermostatted oil-bath at 175 °C for *ca.* 50 h. The liquid product was analysed by g.l.c. and shown to contain three major components (34, 48, and 12.5% composition). Separation was carried out by preparative scale g.l.c. (di-isodecyl phthalate; 95 °C), to give, in order of increasing retention time, *perfluoro-2-ethyl-3,6-di-isopropyl-4,5-dimethylpyridine* (8), b.p. 190 °C (Found: F, 71.0%; *M*, 669. $C_{15}F_{25}N$ requires F, 71.0%; *M*, 669), ^{19}F δ 78.8 (2-CF$_2$CF_3), 108.3 (2-CF_2CF$_3$), 69.1 [3-CF(CF_3)$_2$], 153.1 [3-CF(CF$_3$)$_2$], 52.1 (4- and 5-CF$_3$), 72.4 [6-CF(CF_3)$_2$], and 179.9 p.p.m. [6-CF(CF$_3$)$_2$] (for J values see Scheme 3); *perfluoro-2-ethyl-5,6-di-isopropyl-3,4-dimethylpyridine* (6), m.p. 26 °C (Found: F, 71.1%; *M*, 669), ^{19}F δ 80.3 (2-CF$_2$CF_3), 108.3 (2-CF_2CF$_3$), 51.4 and 53.6 (3- and 4-CF$_3$), 69.0 [5-CF(CF_3)$_2$], 151.3 [5-CF(CF$_3$)$_2$], 71.7 [6-CF(CF_3)$_2$], and 178.1 p.p.m. [6-CF(CF$_3$)$_2$] (for J values see Scheme 3); and *perfluoro-3-ethyl-2,6-di-isopropyl-4,5-dimethylpyridine* (7), m.p. 71—72 °C (Found: F, 70.7%; *M*, 669), ^{19}F δ 72.2 [2-CF(CF_3)$_2$], 178.4 [2-CF(CF$_3$)$_2$], 71.3 (3-CF$_2$CF_3), 80.6 and 90.1 (3-CF_2CF$_3$), 51.9 (4- and 5-CF$_3$), 72.2 [6-CF(CF_3)$_2$], and 179.6 p.p.m. [6-CF(CF$_3$)$_2$] (for J values see Scheme 3).

Pyrolysis of a mixture containing (4) and (5) in the ratio 45 : 55 (by ^{19}F n.m.r.) at 176 °C for 119 h, gave a mixture containing pyridine derivatives (8), (6), and (7) in the ratio 38 : 41 : 15.5, respectively (by g.l.c.–mass spectrometry).

Pyrolysis of Perfluoro-2,4,6-tri-isopropyl-3,5-dimethyl-1-azatetracyclo[2.2.0.0^{2,6}.0^{3,5}]*hexane* (16).—The azaprismane

derivative (16) (0.35 g), in a tube sealed under vacuum, was heated at 174—178 °C for 31 h. Analysis of the product showed the presence of (16) (17.5%), a new pyridine derivative (17) (80%), and some unidentified material. Preparative-scale g.l.c. (silicone elastomer; 100 °C) gave *perfluoro-2,3,6-tri-isopropyl-4,5-dimethylpyridine* (17), m.p. 41 °C (Found: F, 71.5%; *M*, 719. $C_{16}F_{27}N$ requires F, 71.35%; *M*, 719), ^{19}F δ 72.7 [2-CF(CF_3)$_2$], 179.8 [2-CF(CF$_3$)$_2$], 69.8 [3-CF(CF_3)$_2$], 152.1 [3-CF(CF$_3$)$_2$], 50.7 and 52.6 (4- and 5-CF_3), 73.3 [6-CF(CF_3)$_2$], and 180.8 p.p.m. [6-CF(CF$_3$)$_2$] (for *J* values see Scheme 6).

Pyrolysis of Perfluoro-4-ethyl-2,6-di-isopropyl-3,5-dimethyl-1-azabicyclo[2.2.0]*hexa-2,5-diene* (3).—The *para*-bonded species (3) (1.0 g), in a tube sealed under vacuum, was heated at 175 °C for 38 h. A solid (0.4 g) appeared on cooling, which was filtered off and shown by comparison of spectra to be the pyridine derivative (1). The filtrate was shown by g.l.c. to be a mixture of compounds (3) (0.5 g) and (1) (0.1 g).

U.v. spectra

Compound	λ/nm (log $\varepsilon_{max.}$)
(3)	212 (2.47)
(8)	217, 283 (3.89, 3.09)
(6)	217, 280 (3.85, 3.15)
(7)	215, 275 (3.85, 3.15)
(17)	218, 285 (3.89, 3.13)

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