Valence-bond Isomer Chemistry. Part IV.[1a] The Valence-bond Isomers of Pentakis(pentafluoroethyl)pyridine [1b]

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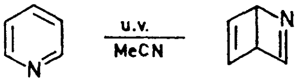
Reaction of pentafluoropyridine with tetrafluoroethylene and caesium fluoride in dimethylformamide produces, *inter alia,* perfluoro-4-ethyl-, -2,4-diethyl-, -2,4,5-triethyl-, -2,3,4,6-tetraethyl-, and -pentaethyl-pyridines. In perfluoro-n-pentane solution, the last compound is isomerized by u.v. light to pentakis(pentafluoroethyl)-1-azabicyclo[2,2,0]hexa-2,5-diene, which in turn forms the corresponding 1-azatetracyclo[2,2,0,0^{2,6},0^{3,5}]hexane. These valence-bond isomers show substantial thermal resistance to rearrangement; in hexafluorobenzene solution, the half-life at 170°C of the hexadiene is 104 h and that of the hexane is 1·1 h.

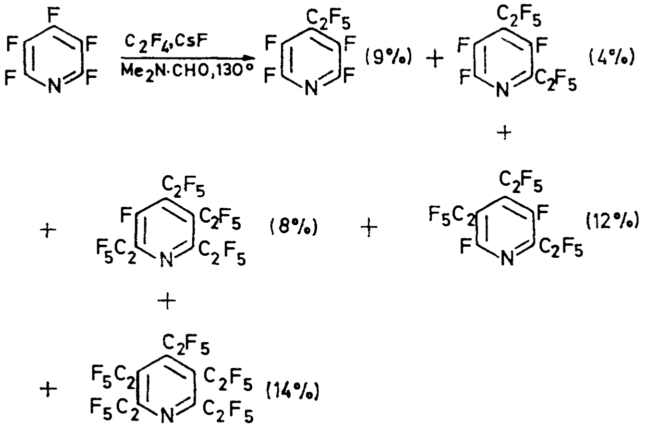
PHOTOCHEMICAL isomerization of benzene derivatives provides a convenient route to the non-planar valence-bond isomers, *para*-bonded benzenes (bicyclo[2,2,0]hexa-2,5-dienes), benzvalenes (tricyclo[3,1,0,0^{2,6}]hex-3-enes), and prismanes (tetracyclo[2,2,0,0^{2,6},0^{3,5}]hexanes). Perfluoroalkylation leads to increased thermal stability, and the hexakis-trifluoromethyl and -pentafluoroethyl derivatives are the most stable examples known.[2]

Little is known concerning the valence-bond isomers of six-membered nitrogen heterocycles. *N*-Methyl-2-pyridone forms a *para*-bonded isomer upon u.v. irradiation in solution,[3] the isomeric picolines and lutidines are photochemically interconvertible in the gas phase, possible *via* prismane intermediates,[4] and it has recently been reported that pyridine is isomerized to an unstable *para*-bonded isomer (Scheme 1) which decays back to pyridine with a half-life of 2·5 min at 25 °C.[5]



SCHEME 1

Nucleophilic displacement of fluoride in perfluoroaromatic compounds by perfluorocarbanions (from fluoro-olefins and casium fluoride in aprotic solvent) provides a convenient route to perfluoroalkyl derivatives.[6] Pentafluoropyridine has been reported to react with tetrafluoroethylene to give low yields of pentakis-(pentafluoroethyl)pyridine,[6,7] together with perfluoroethylpyridines, $C_5F_n(C_2F_5)_{5-n}N$ ($n = 1$—4).[7] We find that reaction in dimethylformamide at 130 °C produces pentafluoroethyl-derivatives (Scheme 2) together with less volatile material. The formation of the 2,4,5-trisubstituted derivative, the product of kinetic rather than thermodynamic control,[8] is in contrast to the earlier report,[7] where the 2,4,6-isomer was claimed, but in accord with a recent communication.[9]



SCHEME 2

Pentakis(pentafluoroethyl)pyridine (I) absorbs in the u.v. region at 209—210 (ε 8540) (hexane) and 269 nm (1340), and its ^{19}F n.m.r. spectrum, which in particular shows non-equivalent geminal fluorine atoms of the 3- and 5-difluoromethylene groups, indicates that rotation

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[1] (*a*) Part III, M. G. Barlow, R. N. Haszeldine, W. D. Morton, and D. R. Woodward, *J.C.S. Perkin I*, 1972, 2170; (*b*) preliminary communication M. G. Barlow, J. G. Dingwall, and R. N. Haszeldine, *Chem. Comm.*,1970, 1580.

[2] See M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc.* (*C*), 1970, 1232, and references quoted therein; D. M. Lemal and L. H. Dunlap, *J. Amer. Chem. Soc.*, 1972, **94**, 6562.

[3] E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, 1964, **86**, 950.

[4] S. Caplain and A. Lablache-Combier, *Chem. Comm.*, 1970, 1247.

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

[6] R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, *J. Chem. Soc.* (*C*), 1968, 2221.

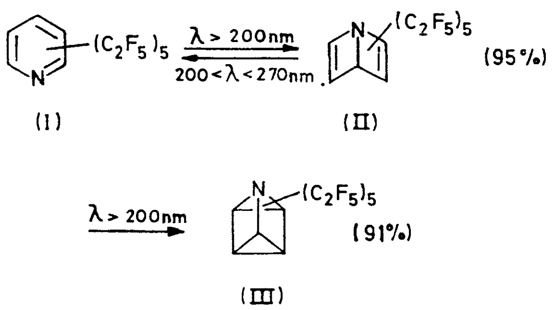
[7] H. C. Fielding, B.P. 1,133,492/1968.

[8] C. J. Drayton, W. T. Flowers, and R. N. Haszeldine, *Chem. Comm.*, 1970, 662; R. D. Chambers, R. P. Corbally, J. A. Jackson, and W. K. R. Musgrave, *ibid*, 1969, 127.

[9] R. D. Chambers, R. P. Corbally, M. Y. Gribble, and W. K. R. Musgrave, *Chem. Comm.*, 1971, 1345.

of the pentafluoroethyl groups is hindered. Irradiation ($\lambda > 270$ nm) of its solution in perfluoro-n-pentane at 35 °C gives a *para*-bonded valence-isomer (II). Light of >200 nm produces the corresponding prismane (III), and isomer (II) is apparently an intermediate in the reaction (Scheme 3).

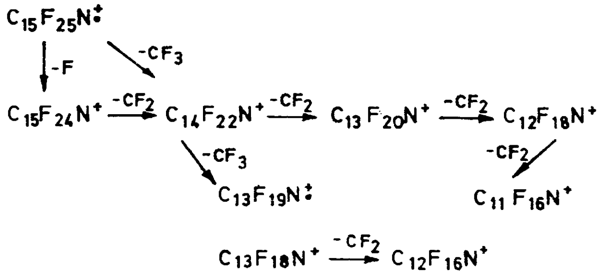
Pentakis(pentafluoroethyl)-1-azabicyclo[2,2,0]hexa-2,5-diene (II) is a colourless liquid, b.p. 176°C, $\nu_{max.}$ 1691 cm^{-1} (C⁚C str.). The ^{19}F n.m.r. spectrum shows three types of pentafluoroethyl group in the ratio 2 : 2 : 1.



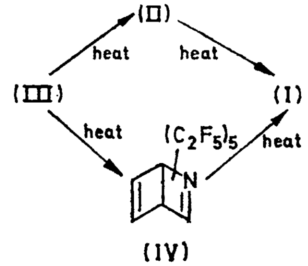
SCHEME 3

Pentakis(pentafluoroethyl)-1-azaprismane (III) is a colourless liquid, b.p. 184 °C, which shows no absorptions at frequencies >1410 cm^{-1}. The ^{19}F n.m.r. spectrum shows three types of pentafluoroethyl group in the ratio 2 : 2 : 1. The mass spectra (at 70 eV) of the pyridine (I) and its two isomers show many similarities. The parent ion is prominent, that of the *para*-bonded isomer being most intense and that of the prismane (III) the weakest. Ions corresponding to loss of F and CF_3 are prominent, the latter being the base peak in the spectra of all three isomers. Metastable ions indicate that the partial fragmentation pattern shown in Scheme 4 is common to all, where elimination of CF_2 is prevalent.

The two valence-bond isomers of pyridine (I) show substantial resistance to thermal rearrangement. In hexafluorobenzene solution (20% w/w) at 170 °C, the *para*-bonded isomer (II) is converted into the pyridine (I) with a half-life of 104 h, and the azaprismane, which has a half-life of 1·1 h, is converted into isomers (II) and (I), together with an additional unidentified compound, which forms the pyridine (I) on further heating. The pyridine (I) is formed in amounts too great for it to be produced solely *via* isomer (II), and it may be that the unidentified compound is the less stable 2-azabicyclo-[2,2,0]hexa-2,5-diene (IV), formed by C–N rather than C–C bond cleavage in prismane (III) (Scheme 5) but attempts to isolate it have so far failed.



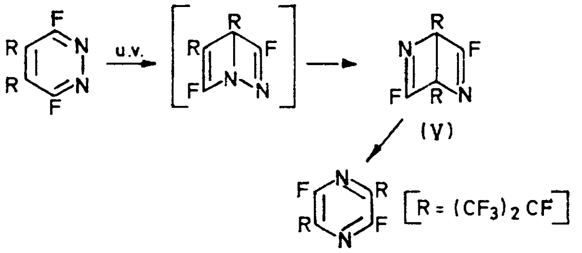
SCHEME 4



SCHEME 5

Perfluoro-2,4,5-triethyl- and -2,3,4,6-tetraethylpyridines both contain adjacent bulky pentafluoroethyl groups, whose steric strain will be relieved in non-planar valence-isomers. However, upon u.v. irradiation, both in perfluoro-n-pentane solution (>200 or >270 nm) and in the vapour phase (>270 nm), they did not isomerize.

The foregoing valence-bond isomers represent the first such examples of pyridine derivatives to be isolated, although 2-azabicyclo[2,2,0]hexa-2,5-diene has been identified chemically and spectroscopically as the unstable product of irradiation of pyridine at 254 nm.[5] Valence-bond isomers have been postulated as intermediates in the photochemical isomerization of polyfluoropyridazines to pyrazines,[10] and recently the *para*-bonded isomer (V) has been identified in the isomerization of perfluoro-4,5-di-isopropylpyridazine to 2,5-di-isopropylpyrazine.[11]



EXPERIMENTAL

Volatile materials were manipulated in a Pyrex vacuum system. Products were identified by elemental analysis, i.r. spectroscopy (Perkin-Elmer model 257), u.v. spectroscopy (Hilger and Watts Ultrascan or Unicam SP 700), ^{19}F n.m.r. spectroscopy (Perkin-Elmer R10 or Hitachi–Perkin-Elmer R20A operating at 56·4 MHz; positive values of chemical shifts are in p.p.m. to high field of external trifluoroacetic acid), mass spectrometry (A.E.I. MS902 at 70 eV), and g.l.c. (Pye 104 for both analytical and preparative separation).

Perfluoro-n-pentane was obtained from the electrochemical fluorination of pyridine,[12] and pentafluoropyridine

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[10] C. G. Allison, R. D. Chambers, Yu. A. Cheburkov, J. A. H. MacBride, and W. K. R. Musgrave, *Chem. Comm.*, 1969, 1200; R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *ibid.*, 1970, 739; D. W. Johnson, V. Austel, R. S. Field, and D. M. Lemal, *J. Amer. Chem. Soc.*, 1970, **92**, 7505.

[11] R. D. Chambers, W. K. R. Musgrave, and K. C. Srivastava, *Chem. Comm.*, 1971, 264.

[12] R. E. Banks, A. E. Ginsberg, and R. N. Haszeldine, *J. Chem. Soc.*, 1961, 1740.

from the reaction of potassium fluoride with pentachloropyridine.[13]

U.v. irradiations were carried out with a Hanovia U.V.S. 500 medium-pressure mercury lamp.

Reaction of Pentafluoropyridine with Tetrafluoroethylene and Caesium Fluoride.—Initial investigation of this reaction was carried out by M. G. Barlow, W. T. Flowers, R. N. Haszeldine, R. Hubbard, and C. Vallance. The following experimental details arise from many subsequent experiments which made possible full product identification. Anhydrous caesium fluoride (2 g), pentafluoropyridine(10·0 g, 60 mmol), and tetrafluoroethylene (25 g, 250 mmol), in dimethylformamide (40 ml), were heated in a stainless steel autoclave at 130 °C for 8 h. Unchanged tetrafluoroethylene (2·0 g, 20 mmol, 8% recovery) was removed, the residue was poured into water (200 ml), and the lower organic layer was separated, washed with water, dried (Na_2SO_4), and distilled *in vacuo* to give crude product (27·2 g). Material (9·4 g) volatile at room temperature *in vacuo* was removed, and diethyl ether (20 ml) was added to the semi-solid residue. The mixture was stirred, cooled to 0 °C, and filtered to give pentakis(pentafluoroethyl)pyridine (5·6 g, 8·4 mmol, 14%) [Found: *M* (mass spec.), 669. Calc. for $C_{15}F_{25}N$: *M*, 669], as white needles, m.p. 74—75 °C (lit.,[6] 77—78 °C), $\lambda_{max.}$ (hexane) 209—210 (log ε 3·93) and 269 (3·13) nm. The filtrate, upon cooling to −78 °C, gave further crystals (0·4 g); removal of the diethyl ether gave an oily residue ,which was a highly complex (g.l.c.) mixture of components.

The material (40 g) volatile at room temperature from four similar reactions was distilled at atmospheric pressure on a spinning-band column to give the following fractions: (i) b.p. 83—103 °C (1·1 g), (ii) 103—114° (2·7 g), (iii) 114—117° (1·4 g), (iv) 117—138° (1·4 g), (v) 138—149° (1·9 g), (vi) 149—160° (2·4 g), (vii) 160—165° (6·6 g), (viii) 165—178° (3·5 g), (ix) 178—183° (5·6 g), and (x) a residue (12·7 g), which was distilled at 20 mmHg [Vigreux column (10 cm)] to give the further fractions: (xi) b.p. 92—98° (2·5 g), (xii) 98—103° (4·8 g), (xiii) 103—106° (1·1 g), and (xiv) a residue (4·1 g).

The various fractions were examined by g.l.c. [trixylyl phosphate (T.X.P.); 3·5 m; 100 °C] and ^{19}F n.m.r. spectroscopy, which indicated the compositions: fraction (i) pentafluoropyridine (100%); (iii) perfluoro-(4-ethylpyridine) (96%); (v) perfluoro-(2,4-diethylpyridine) (75%); (vii) perfluoro-(2,4,5-triethylpyridine) (85%); and (ix) perfluoro-(2,3,4,6-tetraethylpyridine) (90%). Intermediate fractions (ii), (iv), (vi), and (viii) were largely appropriate mixtures of these compounds, and fractions (xi)—(xiv) were highly complex mixtures.

Preparative g.l.c. (T.X.P.; 5 m; 100 °C) gave pure samples of the following: (i) *perfluoro-*(4-*ethylpyridine*) [Found: C, 31·3%; *M* (mass spec.), 269. C_7F_9N requires C, 31·3%; *M*, 269], b.p. 115 °C (Siwoloboff); (ii) *perfluoro-*(2,4-*diethylpyridine*) (Found: C, 29·6; N, 3·5%; *M*, 369. $C_9F_{13}N$ requires C, 29·3; N, 3·8%; *M*, 369), as a colourless liquid, b.p. 139 °C; (iii) *perfluoro-*(2,4,5-*triethylpyridine*) (Found: C, 28·2; N, 2·8%; *M*, 469. $C_{11}F_{17}N$ requires C, 28·2; N, 3·0%; *M*, 469), as a colourless liquid, b.p. 162 °C; and (iv) *perfluoro-*(2,3,4,6-*tetraethylpyridine*) (Found: C, 27·5; N, 2·8%; *M*, 569. $C_{13}F_{21}N$ requires C, 27·4; N, 2·5%; *M*, 569), as a colourless liquid, b.p. 178 °C. ^{19}F N.m.r. chemical shifts are summarized in Table 1. The position of substitution was readily determined by the following considerations: (i) the presence or absence of a low-field absorption associated with ring 2- and 6-fluorines;[14] and (ii) the presence of or absence of a low-field shift of ring fluorine upon replacement of a fluorine by a pentafluoroethyl group *ortho* (by 24·4 ± 2·9 p.p.m.) or *para* (by 11·6 ± 2·3 p.p.m.) to it. Replacement of a fluorine atom by a pentafluoroethyl group also caused a substantial low-field shift of absorptions due to an adjacent pentafluoroethyl group, the effect being most pronounced for the CF_2 absorptions, and when two pentafluoroethyl groups were adjacent.

TABLE 1

^{19}F N.m.r. spectra of perfluoro(ethylpyridine)s

Compound	Chemical shifts [d]				
	δ_2	δ_3	δ_4	δ_5	δ_6
4-C_2F_5 [a]	11·7	63·8	9·4 36·2	63·8	11·7
2,4-$(C_2F_5)_2$ [a]	7·8 39·7	42·3	9·2 36·1	48·9	6·8
2,4,5-$(C_2F_5)_3$ [a,b]	7·0 40·0	40·0	5·1 27·1	5·1 27·1	−20·5
2,3,4,6-$(C_2F_5)_4$ [a]	2·8 30·6	−4·4 11·3	3·4 24·2	30·6	6·6 39·3
2,3,4,5,6-$(C_2F_5)_5$ [c]	3·0 31·0	−5·4 $\left.\begin{matrix}7·4\\14·4\end{matrix}\right\}$ [e]	−6·2 6·3	−5·4 $\left.\begin{matrix}7·4\\14·4\end{matrix}\right\}$	3·0 31·0

[a] Neat liquid. [b] For a solution in acetone (20% w/w) the degeneracy of the 2-CF_2 and 3-F absorptions is removed, bands appearing at 39·4 (CF_2) and 42·3 (CF). [c] 40% (w/w) in acetone. [d] Where two values are recorded, the upper value refers to the CF_3- and the lower value to the CF_2-absorption. [e] AB-type multiplet with J_{AB} *ca.* 300 Hz.

Irradiation of Pentakis(pentafluoroethyl)pyridine in Perfluoro-n-pentane.—(a) *In silica.* Pentakis(pentafluoroethyl)-pyridine (I) (0·669 g, 1·00 mmol) and perfluoro-n-pentane (1 g), sealed *in vacuo* in a silica n.m.r. tube, were irradiated at 35 °C for 400 h at 20 cm from the lamp; the pyridine, which initially was not completely soluble, had then all dissolved. Fractionation of the products *in vacuo* gave unchanged pyridine containing a trace of yellow oil (total 0·047 g), condensing at 20 °C, and *pentakis*(*pentafluoroethyl*)-1-*azatetracyclo*[2,2,0,$0^{2,6}$,$0^{3,5}$]*hexane* (III) (0·610 g, 0·91 mmol, 91%) (Found: C, 27·0%: *M*, 669. $C_{15}F_{25}N$ requires C, 26·9%; *M*, 669) as a colourless liquid, b.p. 184 °C, which condensed at −45 °C.

A similar reaction mixture, examined by ^{19}F n.m.r. spectroscopy after 240 h, was found to comprise (approximately) unchanged pyridine (40%), azaprismane (30%), and *para*-bonded isomer (see below; 30%).

(b) *Pyrex filter.* Pentakis(pentafluoroethyl)pyridine (0·669 g, 1·00 mmol) and perfluoro-n-pentane (1 g), sealed *in vacuo* in a silica n.m.r. tube, were irradiated for 250 h at 20 cm from the lamp with light of wavelength >270 nm (cut-off of a 1·0 mm Pyrex filter). Fractionation of the products *in vacuo* gave unchanged pyridine (0·020 g, 0·03 mmol, 3% recovery) and *pentakis*(*pentafluoroethyl*)-1-*azabicyclo*[2,2,0]*hexa*-2,5-*diene* (II) (0·632 g, 0·95 mmol, 95%) (Found: C, 27·0; N, 2·1%; *M*, 669. $C_{15}F_{25}N$ requires C, 26·9; N, 2·1%; *M*, 669) as a colourless liquid, b.p. 176 °C, which condensed at −45 °C.

Physical Properties of the Valence-bond Isomers of Pentakis-

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[13] R. E. Banks, R. N. Haszeldine, J. V. Latham, and I. M. Young, *J. Chem. Soc.*, 1965, 594; R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *ibid.*, 1964, 3573.

[14] J. Lee and K. G. Orrell, *J. Chem. Soc.*, 1965, 582.

TABLE 2

Mass spectra of the valence-bond isomers of pentakis-(pentafluoroethyl)pyridine *

	Ion			Relative intensities (%)		
m/e	C	F	N	(I)	(II)	(III)
669	15	25	1	10	12·7	6
650	15	24	1	45·6	54·5	47·5
600	14	22	1	100	100	100
562	14	20	1	1	2·7	1·5
550	13	20	1	9	27·2	25
531	13	19	1	1	2·4	2·5
512	13	18	1	3·8	4·2	4
500	12	18	1	3·7	7·6	9·2
481	12	17	1	0·7	2·4	2·2
462	12	16	1	4·9	6·7	7·0
455	13	15	1	0·5	1·2	10
450	11	16	1	1·3	4·2	4·7
412	11	14	1	4·1	6·7	6·2
405	12	13	1	0·7	1·8	6·5
400	10	14	1	0·5	1·8	2·0
374	11	12	1	1·3	1·5	1·5
367	12	11	1	1·1	2·4	5·5
362	10	12	1	1·0	2·1	3·2
355	11	11	1	2·0	3·3	2·7
336	11	10	1	0·5	1·2	1·5
324	10	10	1	1·3	1·8	1·7
317	11	9	1	2·5	4·8	8·2
305	10	9	1	1·0	1·5	1·7
286	10	8	1	0·5	1·2	1·5
274	9	8	1	1·0	1·8	1·5
267	10	7	1	3·0	5·7	7·5
255	9	7	1	6·0	1·2	1·5
248	10	6	1	0·7	1·5	1·7
243	8	7	1	3·0	8·8	5·0
229	10	5	1	1·0	1·2	1·2
224	8	6	1	0·9	1·8	1·7
217	9	5	1	1·5	3·0	3·2
205	8	5	1	0·6	1·5	1·2
198	9	4	1	0·6	1·2	1·2
193	7	5	1	1·0	4·5	4·0
181	6	5	1	0·3	0·9	1·5
179	9	3	1	1·0	1·8	1·5
169	5	5	1	1·3	3·0	3·5
167	8	3	1	0·9	2·4	2·0
155	7	3	1	0·7	2·1	2·0
148	8	2	1	1·0	2·4	2·5
143	6	3	1	1·3	5·1	4·5
131	3	5		0·9	2·1	3·0
124	4	4		1·0	3·6	3·7
119	2	5		11·0	29·0	38·2
100	2	4		1·6	3·6	5·5
93	3	3		0·6	1·8	17·5
69	1	3		32·4	66·5	92·5

* Direct insertion at 150 °C.

Metastables:

Found:		Calc.
554	$650^+ \longrightarrow 600^+ + CF_2$	554·2
538	$669^{+\cdot} \longrightarrow 600^+ + CF_3$	538·5
504	$600^+ \longrightarrow 550^+ + CF_2$	504·4
470	$600^+ \longrightarrow 531^{+\cdot} + CF_3$	470·0
455	$550^+ \longrightarrow 500^+ + CF_2$	454·6
417	$512^+ \longrightarrow 462^+ + CF_2$	417·0
405	$500^+ \longrightarrow 450^+ + CF_2$	405·0

(pentafluoroethyl)pyridine.—Mass spectral data are shown in Table 2.

Pentakis(pentafluoroethyl)-1-azabicyclo[2,2,0]hexa-2,5-diene shows $\nu_{max.}$ (film) 1691m (C=C str.), 1334s, 1310s, 1220vs, 1204vs,sh, 1181s, 1161sh, 1145s, 1123sh, 1114s, 1098s, 1005s, 983s, 935m, 915s, 904sh, 810w, 763m, 751s, 726w, 709sh, 701w, 688w, and 670w cm^{-1}. Its ^{19}F n.m.r. spectrum (in C_6F_6) shows three types of pentafluoroethyl group, δ 5·1 (bridgehead CF_3), 7·3 (CF_3 groups at the C:C bond), 38·7 (bridgehead CF_2), and 35·3 and 43·9 (CF_2 groups at the C:C bond).

Pentakis(pentafluoroethyl)-1-azatetracyclo[2,2,0,0^{2,6},0^{3,5}]-hexane shows $\nu_{max.}$ (film) 1410w, 1340sh, 1332s, 1320sh, 1304sh, 1225vs, 1192vs, 1172vs, 1112vs, 1071m, 1039m, 1015s, 1002sh, 993s, 963m, 942s, 913m, 891m, 849w, 820w, 795w, 758s, 749s, and 697w cm^{-1}; ^{19}F δ (C_6F_6) δ 5·5 (6F), 6·1 (9F), 35·6 (4F, AB-type m, J_{AB} *ca.* 290 Hz, $\delta_A - \delta_B$ 3·1 p.p.m.), 40·1 (4F), and 45·8 (2F, CF_2 at C-4).

Thermal Stability of the Valence-bond Isomers of Pentakis-(pentafluoroethyl)pyridine.—The individual isomers, as *ca.* 20% w/w solutions in hexafluorobenzene, were sealed in thick-walled Pyrex n.m.r. tubes and heated at 170 °C; the tubes were periodically examined, at 35 °C, by ^{19}F n.m.r. spectroscopy. The *para*-bonded isomer (II) rearranged to the extent of 13% to the pyridine during 21 h (half-life 104 h). The azaprismane (III) rearranged to the extent of 71% during 2 h, and produced *para*-bonded isomer (26%), pyridine (30%), and an unidentified component (15%), ^{19}F δ 1·4, 3·7, 38·0, and 41·3 p.p.m. (other bands probably masked by the absorptions of the remaining components). Its half-life is 1·1 h. The unidentified component rearranged to pyridine on further heating.

Attempted Isomerisations of Perfluoro-(2,4,5-*triethylpyridine*) *and* -(2,3,4,6-*tetraethylpyridine*).—(a) *Thermal reactions.* The compounds were passed *in vacuo* through a silica tube (62 × 1·2 cm) packed with silica chips. At 400 °C, the pyridines were recovered unchanged (by i.r.) and at 600 °C slight decomposition (to give perfluoro-n-butane and silicon tetrafluoride) occurred.

(b) *Photochemical reactions.* The pyridines were irradiated as 20% w/w solutions in perfluoro-n-pentane, or in the vapour phase, with u.v. light, and the products were examined by ^{19}F n.m.r. and i.r. spectroscopy. At wavelengths >270 nm no apparent changes occurred, and at wavelengths >200 nm in solution no isomerization was apparent, but a small amount of high-boiling material was formed.

Attempted Reactions of Pentakis(*pentafluoroethyl*)-1-*azabicyclo*[2,2,0]*hexa*-2,5-*diene*.—(a) *With potassium fluoride.* The hexadiene, heated *in vacuo* at 160 °C with a large excess of potassium fluoride for 48 h, gave unchanged hexadiene (78%) and pyridine (I) (20%).

(b) *With furan.* The hexadiene (0·669 g, 1·00 mmol), sealed with a large excess of furan in trichlorofluoromethane (5 ml), was recovered unchanged after 3 weeks at room temperature.

(c) *With bromine.* The hexadiene (0·669 g, 1·00 mmol) and bromine (0·160 g, 1·00 mmol) in trichlorofluoromethane (10 ml), sealed *in vacuo* in a Pyrex ampoule, did not react during 1 week in the dark at room temperature, or during 3 weeks in sunlight.

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