Electrochemical Fluorination. Part I. Electrochemical Fluorination of Alkyl-substituted Pyridines

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Electrochemical fluorination of various alkyl-substituted pyridines affords the corresponding perfluoro-(*N*-fluoroalkylpiperidines) in yields [pyridine (8%), 2-methylpyridine (13%), 3-methylpyridine (2%), 2-ethylpyridine (1%), 2,4-dimethylpyridine (11%), 2,6-dimethylpyridine (26%), 3,5-dimethylpyridine (2%), and 2,4,6-trimethylpyridine (10%)] which depend to a large extent on the position and number of alkyl substituents. Electrochemical fluorination provides a useful route to fluorocarbons of structures corresponding to the original carbon skeletons in the alkylpyridine, together with related fluorocarbons produced by chain degradation. The production of other fluorocarbons reveals that carbon skeleton rearrangement can occur, but to only a minor extent, during electrochemical fluorination.

ELECTROCHEMICAL fluorinations (e.c.f.) of pyridine (8%),[1,2] 2-fluoropyridine (13%),[3] 2-methylpyridine (4%),[4] 3-methylpyridine (2%),[4] 4-methylpyridine (2%),[4] 4-n-propylpyridine (2%),[2] and 4-isopropylpyridine [2] have been reported to afford the corresponding perfluoro-(*N*-fluoropiperidine) derivatives in the yields indicated. The formation of nitrogen trifluoride and perfluorocarbon fractions was noted, but only in the case of the e.c.f. of pyridine was the yield of perfluorocarbon (perfluoro-n-pentane, 27%) reported.[2]

In the present work the e.c.f. of 2,6-dimethylpyridine was examined to determine if, by analogy with pyridine, a reasonable yield of perfluoro-n-heptane could be obtained by loss of ring nitrogen as nitrogen trifluoride, thus providing a useful route to perfluorocarbons whose structure would be determined by the substituents in the pyridine ring. Surprisingly, the major product in the volatile perfluorinated fraction was perfluoro-(*N*-fluoro-2,6-dimethylpiperidine) (IIb) (26%), and although the expected perfluoroheptane was formed it was obtained in lower yield (6%) than anticipated from the earlier pyridine work.

This prompted a study of the e.c.f. of various alkylpyridines in order that the effects of the degree and position of substitution on the products could be determined.

The crude product fractions obtained from the e.c.f. (30 g of substrate) of pyridine and various alkylpyridines are shown in Table 1; the product compositions of the volatile perfluorinated fractions obtained and the isomer distributions of the perfluorocarbons contained therein are shown in Tables 2 and 3, respectively. Reactions were carried out in duplicate or triplicate and gave reproducible results.

TABLE 1

Product fractions from e.c.f. of pyridine and alkylpyridines

Pyridine substituents	Volatile perfluorinated fraction (g)	High-boiling material (g)	Tar (g)
None	45	—	15
2-Me	40	4	14
3-Me	30	<1	18
2-Et	21	1	16
2,4-$(Me)_2$	32	4	35
2,6-$(Me)_2$	42	7	17
3,5-$(Me)_2$	28	2	14
2,4,6-$(Me)_3$	29	9	15

TABLE 2

Major product compositions of volatile perfluorinated fractions

Pyridine substituents	Piperidine	Product yield (%) *	Fluorocarbons † C_5	C_6	C_7
None	(Ia)	8	28		
2-Me	(Ib)	13	2	23	
3-Me	(Ic)	2	4	26	
2-Et	(Id)	1	1	9	8
2,4-$(Me)_2$	(IIa)	11	1	1	20
2,6-$(Me)_2$	(IIb)	26	1	2	6
3,5-$(Me)_2$	(III)	2	1	4	20
2,4,6-$(Me)_3$ ‡	(IIc)	10	1	3	6

* Molar yields based on substrate used; no substrate was recovered. † Trace amounts (<0·5%) of C_3 and C_4 fluorocarbons were also detected. ‡ A mixture of C_8 fluorocarbons (<3%) was also formed which could not be separated satisfactorily.

It has been observed that e.c.f. of the members of an homologous series generally result in decreasing yields of the corresponding perfluorinated derivatives as the chain length is increased, *e.g.* alkanesulphonyl halides.[5] A

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

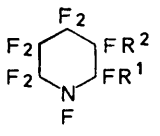
[2] T. C. Simmons and F. W. Hoffmann, *J. Amer. Chem. Soc.*, 1957, **79**, 3429.

[3] R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1962, 3407.

[4] R. E. Banks, J. E. Burgess, and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 2720.

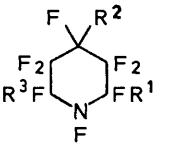
[5] T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 1957, 2640.

similar effect is apparent when chain branching in a substrate is increased.[6] However, Table 2 shows that



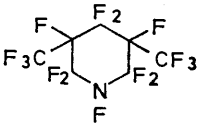
(I)

a; $R^1 = R^2 = F$
b; $R^1 = CF_3, R^2 = F$
c; $R^1 = F, R^2 = CF_3$
d; $R^1 = C_2F_5, R^2 = F$



(II)

a; $R^1 = R^2 = CF_3, R^3 = F$
b; $R^1 = R^3 = CF_3, R^2 = F$
c; $R^1 = R^2 = R^3 = CF_3$



(III)

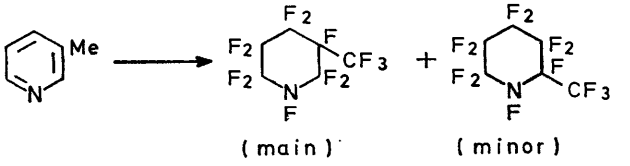
the yields of the perfluoro-(*N*-fluoropiperidine) derivatives *increase* as the hydrogen atoms in the 2- and 6-positions of pyridine are successively replaced by methyl groups. This present result with 2-methylpyridine (13% yield) is in contrast to that reported [4] in which a lower yield of the piperidine (Ib) (4%) was obtained than of the piperidine (Ia) (8%) from pyridine; the yields of the piperidines (Ia and c) formed from pyridine and 3-methylpyridine, respectively, are, however, the same as reported previously.

It has also been reported [3] that e.c.f. of 2-fluoropyridine afforded a higher yield of piperidine (Ia) (13%) than did e.c.f. of pyridine itself. Thus both a 2-fluoro- and a 2-methyl substituent in a pyridine ring inhibit cleavage of the C–N bonds on e.c.f. and it is possible that such methyl substituents sterically protect the C–N bonds.

All the compounds studied which contained 2(6)-methyl groups afforded higher yields of the corresponding piperidine derivatives on e.c.f. than did pyridine. The presence of 4-methyl as a substituent had an adverse effect *cf.* 2-methylpyridine (13%), 2,4-dimethylpyridine (11%), 2,6-dimethylpyridine (26%), and 2,4,6-trimethylpyridine (10%).

3-Methyl substituents gave lower yields of the corresponding piperidine derivatives relative to pyridine or 2-methyl isomers. The low yield from 2-ethylpyridine (1%) was unexpected from the 2-methylpyridine result, but detailed studies of the effect of length of side chain have not yet been made.

The piperidine (Ic) obtained from e.c.f. of 3-methylpyridine contained a small amount of the 2-trifluoromethyl analogue as shown by g.l.c. retention time and n.m.r. and mass spectral data. The reactant 3-methylpyridine was shown not to contain any 2-methylpyridine and so rearrangement had taken place on e.c.f. (Scheme 1).



(main) (minor)

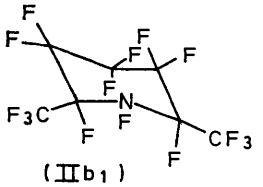
SCHEME 1

The complex ^{19}F n.m.r. spectra of the piperidines (IIa), (IIc), and (III) and g.l.c. indicated that isomeric mixtures were present, but separation of the mixtures into individual components was not achieved. The piperidine (IIb) was separated into two isomers; the major isomer (21%) was identified by ^{19}F n.m.r. spectroscopy (CF_2 signals all present as AB multiplets) as the *cis*-diequatorial conformer (IIb_1) and the minor isomer (5%) is presumably the *trans*-equatorial-axial conformer. A third isomer (4%) of molecular formula $C_7F_{15}N$ with a shorter g.l.c. retention time than those of the two piperidines (IIb) was also isolated. The mass spectra of the two piperidines were almost identical, with base peaks at *m/e* 69 (CF_3^+), but the mass spectrum of the third isomer was markedly different, showing a base peak at *m/e* 119 ($C_2F_5^+$). It is thus suggested that the third isomer is the ring-contracted compound perfluoro-(*N*-fluoro-2-ethyl-5-methylpyrrolidine) (IV).

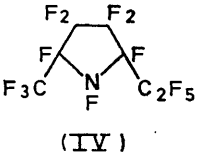
TABLE 3
Isomer composition of perfluorocarbon mixtures

Pyridine substituents	Perfluorocarbons									
	C_5		C_6				C_7				
	n-C_5F_{12}	iso-C_5F_{12}	n-C_6F_{14}	$(CF_3)_2CF{\cdot}C_3F_7$-n	$(C_2F_5)_2CF{\cdot}CF_3$	$[(CF_3)_2CF]_2$	n-C_7F_{16}	$(CF_3)_2CF{\cdot}C_4F_9$-n	$C_2F_5{\cdot}CF(CF_3){\cdot}C_3F_7$-n	$[(CF_3)_2CF]_2CF_2$
None	70	1								
2-Me	19	1	9	1						
3-Me	3	1	1	6						
2-Et	25	1	1	6			40	1		
2,4-$(Me)_2$	1	4	12	11	7	1	0	1	3	
2,6-$(Me)_2$	10	1	8	1			10	1		
3,5-$(Me)_2$		*	1	12				1		7
2,4,6-$(Me)_3$		*	12	12	3	1		1	1	2

* Not determined.



(IIb_1)



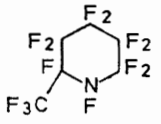
(IV)

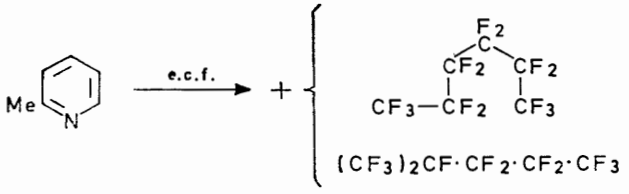
All the other pyridines on e.c.f. gave small amounts (< 0·5%) of mixtures of unidentified compounds with shorter g.l.c. retention times but the same molecular formulae (mass spectrometry) as the corresponding

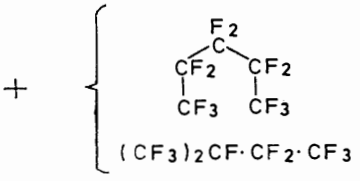
[6] S. Nagase and R. Kojima, *Kogyo Kagaku Zasshi*, 1961, **64**, 1397.

perfluoro-(*N*-fluoropiperidine) derivatives; it is possible that these mixtures contain ring-contracted isomers.

The mono- and di-substituted alkylpyridines with the exception of 2-ethylpyridine on e.c.f. gave, as the major







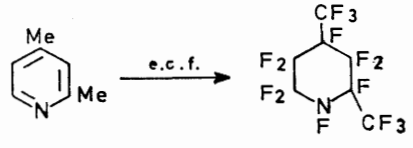
fluorocarbon mixture, that with the same number of carbon atoms as the substrate. Also in all cases the major isomer in the fluorocarbon mixture with the same number of carbon atoms as the substrate had the same carbon skeleton as present in the substrate. This is a convenient route to such fluorocarbons. The yields of the isomeric perfluorocarbons with the same number of carbon atoms as the substrate were dependent on structure. Thus the presence of a 2(6)-ethyl group or two 2(6)-methyl groups (2,6-dimethyl- and 2,4,6-trimethylpyridine) in the substrate resulted in low yields (3—8%), whereas the other pyridines gave reasonable yields (> 20%).

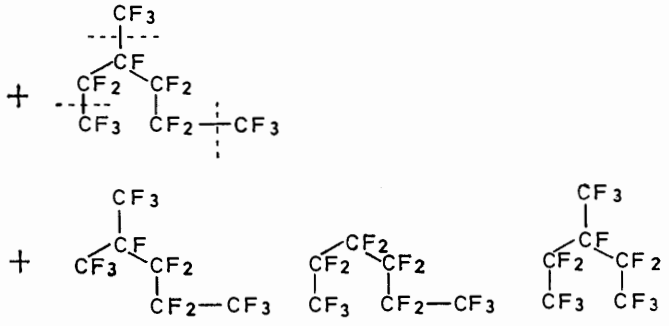
The presence of perfluorocarbon isomers with the same number of carbon atoms as the substrate indicates that skeletal rearrangements are occurring during e.c.f.

The major perfluorocarbon isomers containing one less carbon atom than the substrate generally had the expected structures. Thus 2-methyl- and 2,6-dimethylpyridine afforded mainly perfluoro-n-pentane and perfluoro-n-hexane, respectively, while those substrates containing 3(5)- or 4-methyl groups gave mainly products formed *via* cleavage of the branched methyl groups, *e.g.* 3-methylpyridine gave mainly perfluoro-n-pentane, 3,5-dimethylpyridine gave mainly perfluoro-(2-methylpentane), and 2,4-dimethylpyridine gave a mixture of perfluorohexane isomers in a ratio which indicated that the preferred order of C–C fission was 4-methyl > C_5–C_6 > 2-methyl, *e.g.* Scheme 2.

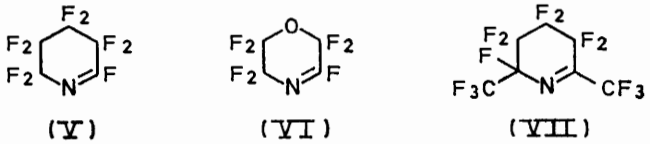
2-Ethyl- and 2,4,6-trimethyl-pyridine were cleaved differently however; the 2-ethyl compound gave perfluoro-(2-methylpentane) as the major C_6 perfluorocarbon rather than the n-isomer, and the 2,4,6-trimethyl compound gave perfluoro-(2,4-dimethylpentane) as the major C_7 isomer with no detectable amount of perfluoro-n-heptane.

Perfluoro-(*N*-fluoropiperidine) and perfluoro-(*N*-fluoromorpholine) [7] are defluorinated by triphenylphosphine to perfluoro-(2,3,4,5-tetrahydropyridine) (V) and perfluoro-(5,6-dihydro-2*H*-1,4-oxazine) (VI), respectively. The piperidine (IIb) as a solution in toluene similarly gave perfluoro-(2,3,4,5-tetrahydro-2,6-dimethylpyridine) (VII) (86%). An attempt further to defluorinate the





SCHEME 2



[7] R. E. Banks, E. D. Burling, B. A. Dodd, and K. Mullen, *J. Chem. Soc.* (*C*), **1969**, 1706.

tetrahydropyridine (VII) to perfluoro-(2,6-dimethylpyridine) by treatment with iron wire at 350 °C gave a complex mixture of unidentified products.

EXPERIMENTAL

The starting pyridine and alkylpyridines were commercial samples which were purified carefully by distillation; their purities were checked by g.l.c. and ^{1}H n.m.r. spectroscopy.

The electrochemical fluorination (e.c.f.) of the various substrates was carried out in a nickel cell (1 l) fitted with a stirrer and which contained seven nickel anodes and seven nickel cathodes placed alternately 2 mm apart. In all experiments the substrate concentration was *ca.* 5%, the total anode area covered by the electrolyte was 10·8 dm^2, the initial current density was *ca.* 1 Adm^{-2} and the experiments were terminated when the current density had dropped to *ca.* 0·1 Adm^{-2}. In other respects the cell and ancillary equipment were as described previously.[8]

In a typical experiment commercial hydrogen fluoride (600 ml) was placed in the cell and dried by electrolysis (4 V for 24 h). After this period pyridine (30 g) was introduced into the cell and electrolysis (6 V) was carried out at room temperature with the cell stirred (200 rev. min.$^{-1}$) until product formation ceased [this prior e.c.f. of pyridine was carried out to check that the cell was performing efficiently and to condition (perhaps activate) the electrodes]. If the prior e.c.f. was satisfactory the substrate under investigation (30 g) was added to the cell and e.c.f. was restarted. When volatile product formation ceased (current density *ca.* 0·1 Adm^{-2}) either more substrate was added and the e.c.f. continued or the experiment was terminated. The volatile perfluorinated product which was evolved from the cell was collected in a cold trap (−78 °C) and any material which was non-condensable at this temperature was allowed to escape. High-boiling material which remained in the cell after reaction was removed *via* a drain tap in the base of the cell. Such high-boiling material invariably contained compounds also present in the volatile perfluorinated fraction and the amount of such material in the high-boiling fraction was determined by distillation followed by g.l.c. and included in the crude weight of volatile perfluorinated product. After this high-boiling material had been removed the amount of tar produced was determined by allowing the hydrogen fluoride to evaporate, and finally drying and weighing the residue.

Products were separated by g.l.c. [10 m Silicone SE 30 oil (20% on Celite) at 20 °C] and identified by elemental analysis, g.l.c., i.r. spectroscopy (Perkin-Elmer model 21 or 257 spectrophotometer), ^{19}F n.m.r. spectroscopy [Perkin-Elmer R10 instrument operating at 56·46 MHz or a Varian HA 100 instrument operating at 94·12 MHz (external reference CF_3CO_2H)], and mass spectrometry (A.E.I. MS 902 instrument). Coupled g.l.c. (as above)–i.r. analysis was carried out with a Wilks Scientific model 41 GC-IR attachment and coupled g.l.c. (as before)–mass spectral analysis was performed with the outlet from the chromatograph connected *via* a Biemann molecular separator to the source inlet of an A.E.I. MS 902 spectrometer.

The e.c.f. of pyridine and the alkylpyridines (30 g) gave product fractions as shown in Table 1. The high-boiling material obtained from all substrates was a complex mixture which could not be separated into its components by g.l.c. or distillation.

The major components of the volatile perfluorinated fractions were separated by g.l.c. (conventional distillation was unsuccessful) and their yields (calculated on relative g.l.c. peak areas) are shown in Table 2.

The perfluoro-(*N*-fluoropiperidine) derivatives obtained from pyridine,[1] 2-methylpyridine,[4] and 3-methylpyridine [4] had i.r. and ^{19}F n.m.r. spectra identical with those reported.[9]

Analytical, b.p., n.m.r., and mass spectral data for the new perfluoro-(*N*-fluoroalkylpiperidines) are given in Table 4.

A second isomer of compound (IIb) (5%) was also isolated which has a slightly longer g.l.c. retention time and its mass spectrum showed peaks at *m/e* 364 [30%, $(M - F)^+$], 314 [51%, $(M - CF_3^+)$], 100 (22%, $C_2F_4^+$), and 69 (100%, CF_3^+), together with other peaks of comparable intensities to those observed in the mass spectrum of the major isomer. The n.m.r. spectrum of the major isomer showed an AB multiplet for the CF_2 group in the 4-position which indicated that it was the diequatorial conformer and so the minor isomer is probably the axial-equatorial conformer. A further compound (4%) with a shorter g.l.c. retention time than the piperidines (IIb) was also isolated and its mass spectrum showed peaks at *m/e* 364 (17%, $C_7F_{14}N^+$), 314 (34%, $C_6F_{12}N^+$), 264 (16%, $C_5F_{10}N^+$), 176 (11%, $C_4F_6N^+$), 131 (10%, $C_3F_5^+$), 119 (100%, $C_2F_5^+$), 114 (10%, $C_2F_4N^+$), 100 (22%, $C_2F_4^+$), and 69 (74%, CF_3^+), which suggested that it was a

TABLE 4

Analytical and spectral data on perfluoro-(*N*-fluoroalkylpiperidines)

Compound	Calc. (%) C	Calc. (%) N	Calc. (%) F	Found (%) C	Found (%) N	Found (%) F	B.p. (°C)	^{19}F N.m.r. chemical shifts * (p.p.m.) and coupling constants (*J*/Hz)	*m/e*
(Id) +			74·4			74·3	96	4·2 (3F, complex, CF_3), 21·5—67·2 (10F, complex, 5 × CF_2), 77·2 (1F, complex, CF)	364 [15%, $(M - F)^+$], 264 [39%, $(M - C_2F_6)^+$], 245 [32%, $(M - C_2F_6)^+$], 100 (63%, $C_2F_4^+$), 69 (100%, CF_3^+)
(IIa)	21·9	3·7	74·4	21·9	3·4	74·0	107	−6·6 (3F, quind, 4-CF_3, 13·7 and 5·6 Hz), −4·9 (3F, ddd, 2-CF_3, 20·9, 15·1, and 13·3 Hz), 20·0—76·0 (6F, complex, 3 × CF_2), 78·0 (2F, complex, 2 × CF)	364 (37%), 314 [49%, $(M - CF_3)^+$], 195 [13%, $(M - C_3F_8)^+$], 100 (41%), 69 (100%)
(IIb$_1$) major isomer	21·9	3·7		22·2	3·7		93	−4·0 (6F, ddd, 2- and 6-CF_3, 21·8, 14·5, and 11·3 Hz), 12·0br (1F, NF), 42·5—68·0 (6F, 2ABm, 3 × CF_2), 78·0 (2F, t, 2 × CF, 17·9 Hz)	364 (38%), 314 (71%), 245 (11%), 100 (30%), 69 (100%)
(III) †	21·9		74·4	22·0		74·5	101	−6·0 (3F, complex, CF_3), −5·6 (3F, complex, CF_3), 24·4—75·5 (6F, complex, 3 × CF_2), 77·5 (2F, complex, 2 × CF)	383 (4%, M^+), 364 (22%), 345 [19%, $(M - F_2)^+$], 195 (19%), 150 (75%, $C_3F_6^+$), 69 (100%)
(IIc) †	22·2	3·2	74·6	22·5	3·6	74·6	122	−7·0 (3F, quind, 4-CF_3, 14·1 and 5·6 Hz), −4·4 (6F, ddd, 2- and 6-CF_3, 21·8, 14·8 and 14·1 Hz), 39·0—42·5 (4F, complex, 2 × CF_2), 75·0 (1F, complex, 4-F), 77·0 (2F, complex, 2- and 6-F)	414 [43%, $(M - F)^+$], 364, [65%, $(M - CF_3)^+$], 245, [20%, $(M - C_3F_8)^+$], 69 (100%)

* Negative values are to low field of reference. † N.m.r. spectra run on capillary samples; because of adverse noise-to-signal ratios absorptions due to N–F were not observed.

[8] T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 1956, 173.
[9] J. Lee and K. G. Orrell, *Trans. Faraday Soc.*, 1967, **63**, 16.

compound of molecular formula $C_7F_{15}N$ with a C_2F_5 group, possibly perfluoro-(*N*-fluoro-2-ethyl-5-methylpyrrolidine).

The C_5, C_6, and C_7 fluorocarbons formed in the e.c.f. experiments were shown by g.l.c. and ^{19}F n.m.r. spectroscopy to be mixtures of isomers the compositions of which are given in Table 3.

The ^{19}F n.m.r. spectrum of perfluoro-(3-methylpentane), showed bands at δ — 5·0 (complex, 3F, CF_3·CF), 5·0 (6F, complex, 2 × CF_3·CF_2), 41·5 (4F, complex, 2 × CF_2), and 109·5 (complex, 1F, CF); that of perfluoro-(3-methylhexane), $\overset{1}{CF_3}\cdot\overset{2}{CF_2}\cdot\overset{3}{CF}(\overset{4}{CF_3})\cdot\overset{5}{CF_2}\cdot\overset{6}{CF_2}\cdot\overset{7}{CF_3}$, showed bands at δ — 5·2 [3F, complex, CF_3(4)], 4·5 [3F, dsex, CF_3(1), $J_{1,3}$ 12·5, J 6·4 Hz], 5·2 [3F, td, CF_3(7), $J_{7,5}$ 12·9, $J_{7,3}$, 1·6 Hz], 37·0 [2F, complex, CF_2(5)], 40·0 [2F, complex, CF_2(2)], 48·0 [2F, complex, CF_2(6)], and 109·2 (1F, complex, CF); that of perfluoro-(2,4-dimethylpentane) showed bands at δ — 7·0 (12F, td, 4 × CF_3, J_{CF_3,CF_2} 12·0, $J_{CF_3,CF}$ 10·1 Hz), 26·5 (2F, nonet, CF_2), and 104·0 (complex, 2F, 2 × CF); and that of perfluoro-n-pentane showed bands at δ 6·0 (6F, ttt, 2 × CF_3, $J_{1,3}$ 10·4, $J_{1,4}$ 2·4, $J_{1,2}$ 1·1 Hz), 47·4 [2F, complex, CF_2(3)], and 50·1 [4F, complex, CF_2(2) and CF_2(4)]; all other perfluorocarbons had n.m.r. spectra identical with those reported, *i.e.* perfluoro-(2-methylbutane),[10] perfluoro-n-hexane,[11] perfluoro-(2-methylpentane),[10,12] perfluoro-(2,3-dimethylbutane),[10,12] perfluoro-n-heptane,[13] and perfluoro-(2-methylhexane).[14]

Reaction of Perfluoro-(N-*fluoro*-2,6-*dimethylpiperidine*) *with Triphenylphosphine* (with R. E. Banks and C. Oppenheim).—The piperidine (30·0 g, 78·0 mmol) was slowly treated with triphenylphosphine (30·0 g, 11·5 mmol) in toluene (100 ml); the mixture was stirred at room temperature (24 h), then distilled to afford *perfluoro*-(2,3,4,5-*tetrahydro*-2,6-*dimethylpyridine*) (23·0 g, 67·0 mmol, 86%) (Found: C, 24·4; N, 4·3; F, 71·6. $C_7F_{13}N$ requires C, 24·3; N, 4·1; F, 71·6%), b.p. 72–73 °C; ^{19}F n.m.r. bands at —6·5 (3F, complex, CF_3·C:N), 2·2 (3F, complex, CF_3), 21·0—72·2 (6F, 3 ABmult, 3 × CF_2), and 69·0 p.p.m. (1F, complex, CF); *m/e* 345 (36%, M^+), 276 [24%, $(M - C_2F_3)^+$], 245 [100%, $(M - C_2F_4)^+$], 176 (28%, $C_4F_6N^+$), 131 (24%, $C_3F_5^+$), 119 (24%, $C_2F_5^+$), 100 (44%, $C_2F_4^+$), and 69 (92%, CF_3^+).

Treatment of the tetrahydropyridine with iron wire in a stainless steel autoclave at 350 °C gave complete conversion into a complex mixture of products (fifteen components by g.l.c.); reaction did not occur at or below 300 °C.

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