

## ***N*-Fluoro-compounds. Part IV.<sup>1</sup> Photochemical and Fluoride-initiated Reactions between Perfluoro-*N*-fluoropiperidine and Perfluoropropene<sup>2</sup>**

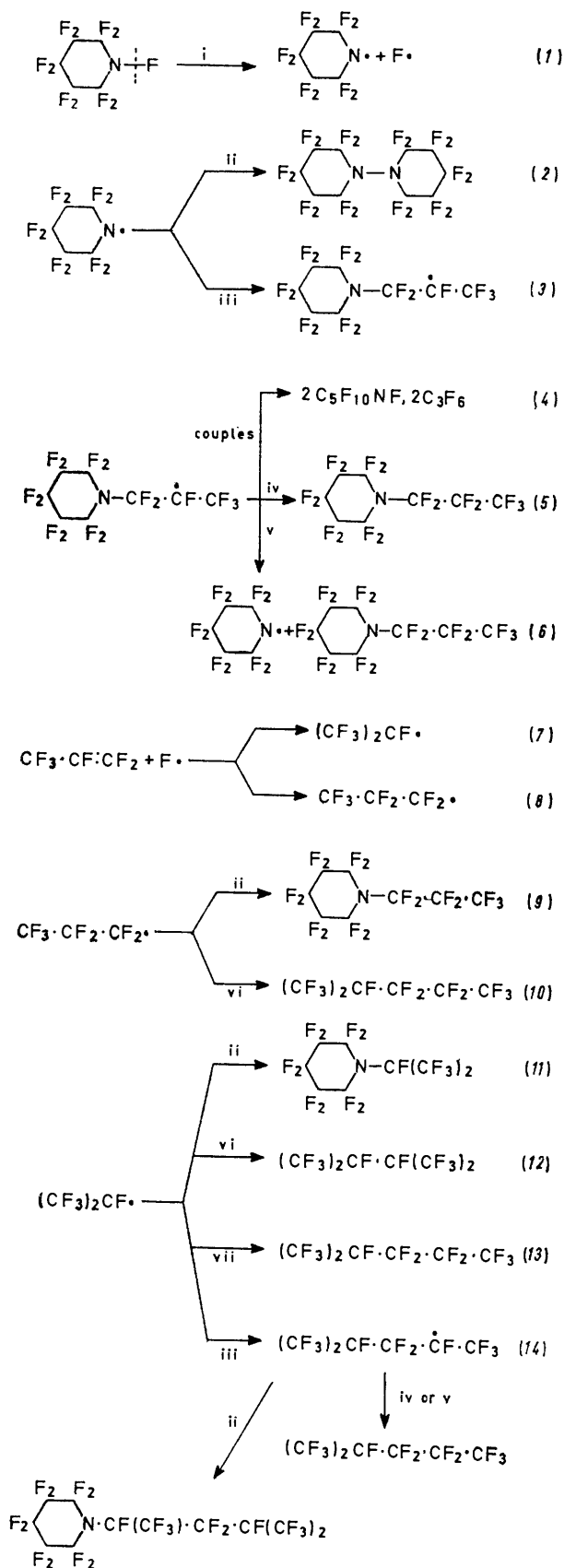
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Photolysis of perfluoro-*N*-fluoropiperidine in the presence of perfluoropropene gives perfluoro-(2-methylpentane), perfluoro-(2,3-dimethylbutane), perfluoro-(*N*-propylpiperidine), perfluoro-(*N*-isopropylpiperidine), perfluoro-[*N*-(1,3-dimethylbutyl)piperidine], a 2:2 adduct ( $2C_5F_{10}NF:2C_3F_6$ ), and perfluoro-*NN'*-bipiperidyl. Thermal reaction of perfluoro-*N*-fluoropiperidine with perfluoropropene in stainless steel in the presence of caesium fluoride yields, *inter alia*, perfluoro-(2-isopropyl-3,4,5,6-tetrahydropyridine) and perfluoro-(2-isopropylpyridine); this conversion is believed to involve defluorination of the piperidine to perfluoro-2,3,4,5-tetrahydropyridine followed by attack on this product by perfluoroisopropyl anion and subsequent aromatisation of perfluoro-(2-isopropyl-3,4,5,6-tetrahydropyridine) thus formed. Perfluoro-(2-isopropylpyridine) can be prepared from perfluoro-*N*-fluoropiperidine in three separate stages according to this scheme, which exemplifies a possible useful route to 2-substituted tetrafluoropyridines.

ULTRAVIOLET irradiation of a gaseous equimolar mixture of perfluoro-*N*-fluoropiperidine and perfluorocyclobutene yields perfluoro-(*N*-cyclobutylpiperidine), perfluorobicyclobutyl, and perfluoro-*NN'*-bipiperidyl (1), a result consistent with a free-radical mechanism initiated by homolysis of the piperidine N-F bond.<sup>1</sup> Similar irradiation of a 1:1 molar mixture of perfluoro-*N*-fluoropiperidine and perfluoropropene gives the bipiperidyl (1) (30%), perfluoro-(*N*-propylpiperidine) (2) (7%), perfluoro-(*N*-isopropylpiperidine) (3) (10%), per-

reaction between perfluoro-*N*-fluoropiperidine and perfluoropropene is analogous to that suggested for the reaction involving perfluorocyclobutene.<sup>1</sup> The steps to be considered are shown in Scheme 1.

The polar character of a free radical R• often determines the relative ease with which it attacks the two non-equivalent olefinic carbon atoms in perfluoropropene, since the radicals  $R\dot{C}F_2\cdot\dot{C}F\cdot CF_3$  and  $R\dot{C}F(CF_3)\cdot\dot{C}F_2$  possess comparable stabilities; steric factors favour formation of the former new radical.<sup>5</sup> Since bistri-



SCHEME 1

methyl radical shows a 4 : 1 preference for attack at the  $\text{CF}_2$  group.<sup>5</sup>

**Thermal Fluoride-initiated Reaction of Perfluoro-*N*-fluoropiperidine with Perfluoropropene.**—The  $^{19}\text{F}$  n.m.r. chemical shift data [see Figure, (a)] for the perfluoro- (*N*-isopropylpiperidine) (3) obtained photochemically are consistent with those published for material synthesised by electrochemical fluorination of *N*-isopropylpiperidine<sup>8</sup> but not with those [see Figure, (b)] reported for a compound believed, on the basis of analytical values, to possess structure (3) and prepared by heating perfluoro-*N*-fluoropiperidine with perfluoropropene and anhydrous caesium fluoride at 200 °C in a stainless steel autoclave.<sup>9</sup> Additionally, the relative intensities quoted<sup>9</sup> for the  $^{19}\text{F}$  n.m.r. absorptions shown by the compound obtained in the last manner clearly do not support structure (3) [cf. Figure, (a) and (b)]. These discrepancies induced us to reinvestigate the fluoride-initiated reaction, and the product thought previously to be perfluoro- (*N*-isopropylpiperidine) was found to be perfluoro- (2-isopropyl-3,4,5,6-tetrahydropyridine) (7) [cf. Figure, (b) and (c)].

The reaction of perfluoro-*N*-fluoropiperidine with perfluoropropene and caesium fluoride occurs only slowly at 200 °C, so an experiment was carried out at 280 °C for 2 days, then, since no marked pressure change was noted, at 330 °C for 3 days in an old autoclave which had seen much service with halogenated compounds. Complete conversion of the *N*-fluoropiperidine into product was achieved and the material boiling above room temperature was shown to contain, *inter alia*, a small amount of perfluoro- (2-isopropyl-3,4,5,6-tetrahydropyridine), perfluoro- (*N*-butyldenemethylamine) and perfluoro- (*N*-methylpyrrolidine) (the products of thermal reorganisation of perfluoro-*N*-fluoropiperidine<sup>10</sup>), and perfluoro- (2-isopropylpyridine), which was isolated by g.l.c. in 29% yield. When the high-temperature experiment was repeated in a fairly new stainless steel autoclave, the volatile product from an equimolar mixture of perfluoro-*N*-fluoropiperidine and perfluoropropene and an excess of anhydrous caesium fluoride contained perfluoropropane (43% based on  $\text{C}_5\text{F}_{10}\text{NF}$ ), perfluoro- (*N*-butyldenemethylamine) (21%), perfluoro- (*N*-methylpyrrolidine) (22%), perfluoro- (2-isopropyl-3,4,5,6-tetrahydropyridine) (43%), and traces of perfluoro- (2-isopropylpyridine). It seems that in the original high-temperature reaction defluorination of perfluoro- (2-isopropyl-3,4,5,6-tetrahydropyridine) to perfluoro- (2-isopropylpyridine) occurred at the inner surfaces of

<sup>8</sup> S. V. Sokolov, A. P. Stepanov, L. N. Pushkina, S. A. Mazalov, and O. K. Shabalina, *Zhur. obshchei Khim.*, 1966, **36**, 1613.

<sup>9</sup> R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Org. Chem.*, 1965, **30**, 3524.

<sup>10</sup> R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1962, 3407.

Reagents: i, u.v. light; ii, perfluoro-*N*-piperidyl radical; iii, perfluoropropene; iv, fluorine atom; v, perfluoro-*N*-fluoropiperidine; vi, perfluoroisopropyl radical; vii, perfluoro-*n*-propyl radical.

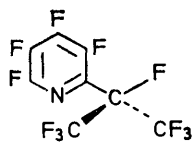
SCHEME 1

the reaction vessel, and this aromatisation has been simulated by heating the tetrahydro-compound in a different stainless steel autoclave containing iron filings at 300 °C for 1 day (see Scheme 2). The apparent

ment on carbon depicted in Scheme 3 is, however, highly unlikely in view of the famed resistance of fluorocarbons to nucleophilic attack, and initial defluorination of perfluoro-*N*-fluoropiperidine at the auto-

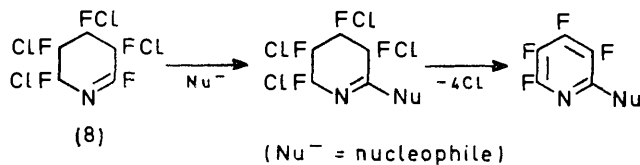
this type of attack has been postulated previously,<sup>13</sup> but never for a reaction involving a perfluorocarbanion.

**2-Substituted Tetrafluoropyridines.**—Perfluoro-(2-isopropylpyridine) is only the second perfluoro-(2-alkylpyridine) to be reported, the other being perfluoro-(2-methylpyridine).<sup>14</sup> At 35 °C its <sup>19</sup>F n.m.r. spectrum shows a large through-space coupling (51.0 Hz) between the 3-fluorine atom and the tertiary fluorine of the side-chain, which suggests that conformation (A) is highly populated; \* similarly, the <sup>19</sup>F spectrum of perfluoro-(2-isopropyl-3,4,5,6-tetrahydro-pyridine) shows a large through-space coupling (33.8 Hz) between the 3-fluorine atoms and the tertiary fluorine of the CF(CF<sub>3</sub>)<sub>2</sub> group. The results of n.m.r. studies on conformational isomers of other perfluoroisopropyl derivatives of perfluoropyridine have been published<sup>16</sup> since the spectrum of perfluoro-(2-isopropylpyridine) was analysed.<sup>17</sup>



(A)

The preparation of perfluoro-(2-isopropylpyridine) by the route shown in Scheme 2 suggests a new approach to the problem of the development of a versatile method of synthesis of 2-substituted tetrafluoropyridines. Use of perfluoro-2,3,4,5-tetrahydro-pyridine as an intermediate, however, demands that the substituent introduced into the 2-position must be capable of withstanding the rather harsh conditions required in the aromatisation step, and a more attractive proposition is outlined in Scheme 6.



SCHEME 6

The 2,3,4,5-tetrachloro-2,3,4,5,6-pentafluorotetrahydro-pyridine (8) required can be procured in high yield by photochlorination of pentafluoropyridine<sup>18</sup> and does revert to the latter when treated with zinc dust in boiling dioxan.<sup>19</sup>

#### EXPERIMENTAL

Perfluoro-*N*-fluoropiperidine was prepared by electrochemical fluorination of pyridine. Perfluoropropene was taken directly from a commercial cylinder (Pennwalt Chemicals Corp.).

\* Full details of the <sup>19</sup>F n.m.r. spectroscopic properties of this compound will be reported later.<sup>15</sup>

<sup>13</sup> R. E. Banks and G. E. Williamson, *Chem. and Ind.*, 1964, 1864; R. E. Banks and E. D. Burling, *J. Chem. Soc.*, 1965, 6077; R. E. Banks, R. N. Haszeldine, and R. Hatton, *Tetrahedron Letters*, 1967, 3993.

<sup>14</sup> R. E. Banks, J. E. Burgess, and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 2720; L. P. Anderson, W. J. Feast, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1969, 2559.

Products were identified by elemental analysis, molecular weight determination (Regnault's method unless stated otherwise), g.l.c. analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometers models 21 and 257), <sup>19</sup>F n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 56.46 MHz and 35 °C), and mass spectrometry (A.E.I. MS/2H or MS902 instrument). Coupled g.l.c.-i.r. analysis was performed with a Wilks Scientific model 41 GC-IR attachment in conjunction with a Perkin-Elmer model 137 (Infracord) spectrophotometer.

**Perfluoro-2,3,4,5-tetrahydro-pyridine** (by R. HATTON).—Perfluoro-*N*-fluoropiperidine (13.6 g, 48.1 mmol) was added slowly (1 h) to a stirred solution of triphenylphosphine (12.6 g, 48.1 mmol) in dry benzene (40 ml) contained in a three-necked flask fitted with a vacuum-jacketed column (25 × 1 cm) packed with nickel Dixon rings and surmounted by a partial take-off head cooled with methanol-solid carbon dioxide. The mixture was stirred for 45 min then distilled, to give perfluoro-2,3,4,5-tetrahydro-pyridine (9.2 g, 37.6 mmol, 78%) (Found: *M*, 245. Calc. for C<sub>5</sub>F<sub>9</sub>N: *M*, 245), b.p. 40 °C (lit.,<sup>10</sup> 40.7 °C), with the expected i.r. spectrum. The distillation residue was cooled and filtered, to give difluorotriphenylphosphorane (12.1 g, 40.3 mmol, 84%) (Found: C, 71.8; H, 4.8; P, 10.3. Calc. for C<sub>18</sub>H<sub>18</sub>F<sub>2</sub>P: C, 72.0; H, 5.0; P, 10.3%), m.p. 140 °C, with the expected i.r. spectrum.

Alternatively, a solution of triphenylphosphine in dry benzene can be added slowly to a stirred mixture of perfluoro-*N*-fluoropiperidine and benzene, as described for defluorination of perfluoro-*N*-fluoromorpholine to perfluoro-5,6-dihydro-2*H*-1,4-oxazine with the phosphine.<sup>20</sup> In either procedure, rapid mixing of the reactants should be avoided; a mild explosion occurred when perfluoro-*N*-fluoropiperidine was added quickly to a solution of triphenylphosphine in benzene.

**Reactions of Perfluoro-*N*-fluoropiperidine.**—(a) **Photolysis with perfluoropropene.**—A gaseous, equimolar mixture of perfluoro-*N*-fluoropiperidine (9.62 g, 34.0 mmol) and perfluoropropene (5.10 g) was irradiated (20 h) with u.v. light in a photochemical reactor (5 l) of the type described previously.<sup>3</sup> A liquid product soon began to collect in the bottom of the reactor, and after only 2 h the pressure had fallen from 240 to 128 mmHg. The gaseous product was shown by i.r. spectroscopy to comprise carbon dioxide, carbonyl fluoride, silicon tetrafluoride, and perfluoropropene. The liquid product (12.2 g) was shown by g.l.c. (4 m silicone MS550 oil-Celite at 98 °C) to contain perfluoro-hexanes (2.72 mmol, 16%), perfluoro-(*N*-isopropyl- and *N*-propyl-piperidine) [(3) and (2)] (60:40 mixture; 5.79 mmol, 17%), perfluoro-*NN'*-bipiperidyl (1) (5.10 mmol, 30%), a 1:2 perfluoro-*N*-fluoropiperidine-perfluoropropene adduct (4) (0.68 mmol, 2%), and several unidentified components. Distillation of the liquid product (11.1 g) in a semi-micro Vigreux still gave: (i) a 52:48 mixture (analysed by <sup>19</sup>F n.m.r. spectroscopy) of perfluoro-(2-methylpentane) (5) and perfluoro-(2,3-dimethylbutane) (6)

<sup>15</sup> M. G. Barlow, in preparation.

<sup>16</sup> R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Chem. Comm.*, 1969, 178; *Tetrahedron*, 1970, 26, 71.

<sup>17</sup> K. Mullen, Ph.D. Thesis, University of Manchester, 1967.

<sup>18</sup> R. E. Banks, W. M. Cheng, R. N. Haszeldine, and G. Shaw, *J. Chem. Soc. (C)*, 1970, 55.

<sup>19</sup> R. E. Banks and C. Oppenheim, unpublished results.

<sup>20</sup> R. E. Banks, E. D. Burling, B. A. Dodd, and K. Mullen, *J. Chem. Soc. (C)*, 1969, 1706.

(0.6 g, 1.8 mmol, 11%) (Found: C, 21.1%; *M*, 336. Calc. for  $C_6F_{14}$ : C, 21.3%; *M*, 338), b.p. 59–61 °C [lit.,<sup>21</sup>  $(CF_3)_2CF\cdot CF_2\cdot CF_2\cdot CF_2\cdot CF_3$ , 58.0 °C; lit.,<sup>22</sup>  $(CF_3)_2CF\cdot CF(CF_3)_2$ , 60.0 °C at 760 mmHg], which was pale blue owing to the presence of traces of perfluoropentamethylene nitroxide; (i) a fraction (2.90 g), b.p. 120–130 °C, which was separated by g.l.c. (4 m Kel-F no. 10 oil–Celite at 103 °C) into perfluoro-*NN'*-bipiperidyl (1) and a 60:40 mixture (analysed by <sup>19</sup>F n.m.r. spectroscopy) of perfluoro-(*N*-isopropylpiperidine) (3) and perfluoro-(*N*-propylpiperidine) (2) (1.78 g, 4.11 mmol, 12%) (Found: C, 22.3; N, 3.6%; *M*, 430. Calc. for  $C_8F_{17}N$ : C, 22.2; N, 3.2%; *M*, 433), b.p. (isotherm) 92.5 °C; (iii) a 4:1 mixture analysed by g.l.c., retention times being checked with authentic samples) of perfluoro-*NN'*-bipiperidyl (1) and perfluoro-[*N*-(1,3-dimethylbutyl)piperidine] (4) (3.60 g), b.p. 163–164 °C; and (iv) a semi-solid residue (2.9 g) with an elemental composition close to that required by a 2:2 perfluoro-*N*-fluoropiperidine–perfluoropropene adduct (Found: C, 23.0; N, 3.7. Calc. for  $C_{16}F_{34}N_2$ : C, 22.2; N, 3.2%). Fractions (ii)–(iv) inclusive gave negative results in N–F tests<sup>5</sup> with sodium iodide in wet acetone.

The experiment was repeated using a 1.0:1.6 molar mixture of perfluoro-*N*-fluoropiperidine (7.21 g, 25.5 mmol) and perfluoropropene (6.16 g, 41.1 mmol). The liquid product (11.6 g) contained (analysed by g.l.c.) perfluoro-(2-methylpentane) (5) and perfluoro-(2,3-dimethylbutane) (6) (19% yield), perfluoro-(*N*-propyl- and -isopropylpiperidine) [(2) and (3)] (15%), perfluoro-*NN'*-bipiperidyl (1) (1%), perfluoro-[*N*-(1,3-dimethylbutyl)piperidine] (4) (10%), and material believed to be a 2:2 perfluoro-*N*-fluoropiperidine–perfluoropropene adduct (9%). Distillation of 10.0 g of this liquid product yielded: (i) a blue liquid (1.00 g), b.p. 58–62 °C, which was shaken with toluene (1 ml) (with which it was immiscible) to remove perfluoropentamethylene nitroxide, to give a 55:45 mixture (analysed by <sup>19</sup>F n.m.r. spectroscopy) of perfluoro-(2-methylpentane) (5) and perfluoro-(2,3-dimethylbutane) (6) (0.95 g, 2.81 mmol, 14% based on  $C_3F_6$ ); (ii) a mixture (2.3 g), b.p. 90–140 °C, shown by g.l.c. to comprise perfluoro-(*N*-isopropylpiperidine) (3) and perfluoro-(*N*-propylpiperidine) (2) (60:40 ratio) and perfluoro-[*N*-(1,3-dimethylbutyl)piperidine] (4); and (iii) perfluoro-[*N*-(1,3-dimethylbutyl)piperidine] (4) contaminated with perfluoro-*NN'*-bipiperidyl (1) (1.3 g), b.p. 150–160 °C. Perfluoro-[*N*-(1,3-dimethylbutyl)piperidine] (4) (1.08 g, 1.85 mmol, 7%) [Found: C, 22.3; N, 2.9%; *M* (mass spec.), 583.  $C_{11}F_{23}N$  requires C, 22.6; N, 2.4%; *M*, 583] was separated from fraction (iii) by g.l.c. (4 m Kel-F no. 10 oil–Celite at 100 °C).

(b) *Reaction with perfluoropropene in the presence of caesium fluoride.* (i) At 200 °C. A mixture of perfluoro-*N*-fluoropiperidine (7.10 g, 25.1 mmol) and perfluoropropene (3.75 g, 25.0 mmol) was heated in a new stainless steel autoclave (100 ml) containing finely powdered anhydrous caesium fluoride (18.0 g, 118 mmol) at 200 °C for 3 days. By a combination of trap-to-trap fractional condensation, *in vacuo*, and coupled g.l.c.–i.r. analysis, the volatile product was shown to contain much unchanged perfluoropropene and perfluoro-*N*-fluoropiperidine (*ca.* 80%) and some perfluoropropane and perfluoro-(2-isopropyl-3,4,5,6-tetrahydropyridine) (7).

(ii) At 280–330 °C. A mixture of perfluoro-*N*-fluoropiperidine (7.10 g, 25.1 mmol), perfluoropropene (3.75 g,

25.0 mmol), and anhydrous caesium fluoride (18.0 g, 118 mmol) was heated at 280 °C in an old, etched, stainless steel autoclave for 2 days and then, since little or no change in pressure had occurred, at 330 °C for 3 days (initial pressure 11 atm, final pressure *ca.* 7 atm). The volatile product was fractionated by passage, *in vacuo*, through a trap cooled to –72 °C into one kept at –196 °C. The –72 °C fraction was distilled to give a complex mixture (1.38 g), b.p. 30–100 °C, containing (by g.l.c. and i.r. analysis) at least seven components, including perfluoro-(*N*-butylidene-methylamine), perfluoro-(*N*-methylpyrrolidine), perfluoro-(2-isopropyl-3,4,5,6-tetrahydropyridine), perfluoro-(2-isopropylpyridine), perfluoropyridine, and perfluoro-(2-methylpent-2-ene), and a fraction (3.36 g), b.p. 120–140 °C; the major component of the last was isolated by g.l.c. (4 m Kel-F oil no. 10–Celite, 100 °C) and found to be perfluoro-(2-isopropylpyridine) (2.33 g, 7.31 mmol, 29%) [Found: C, 30.2; N, 4.1%; *M* (mass spec.), 319.  $C_8F_{11}N$  requires C, 30.1; N, 4.3%; *M*, 319], b.p. 124 °C,  $\lambda_{max}$  (film) 6.76 vs  $\mu m$  (polyfluorinated pyridine nucleus).

When the experiment was repeated in a new stainless steel autoclave with caesium fluoride taken from a different source, the volatile product, examined by a combination of trap-to-trap fractional condensation *in vacuo* and coupled g.l.c.–i.r. analysis, was found to contain perfluoropropene (0.50 g, 3.33 mmol), perfluoropropane (2.00 g, 10.7 mmol), perfluoro-(*N*-butylidene-methylamine) (1.47 g, 5.19 mmol), perfluoro-(*N*-methylpyrrolidine) (1.57 g, 5.55 mmol), perfluoro-(2-isopropyl-3,4,5,6-tetrahydropyridine) (7) (4.23 g, 10.7 mmol), traces of perfluoro-(2-isopropylpyridine), and unidentified high-boiling material (0.58 g).

(c) *Defluorination.* Perfluoro-*N*-fluoropiperidine (1.00 g) contaminated with 10% (w/w) of perfluoro-*n*-pentane was heated at 290 °C for 24 h in a stainless steel autoclave (16 ml) to give perfluoro-2,3,4,5-tetrahydropyridine (0.64 g, 82%), identified by g.l.c., i.r., and n.m.r. analysis.

*Reaction of Perfluoro-2,3,4,5-tetrahydropyridine with Perfluoropropene in the Presence of Caesium Fluoride.*—Perfluoro-2,3,4,5-tetrahydropyridine (2.45 g, 10.0 mmol), perfluoropropene (3.24 g, 21.6 mmol), and anhydrous caesium fluoride (*ca.* 6 g) were heated in a Monel autoclave (50 ml) at 245 °C for 65 h. Distillation of the volatile product gave perfluoro-(2-isopropyl-3,4,5,6-tetrahydropyridine) (7) (1.32 g, 3.34 mmol, 33%) [Found: C, 24.0; N, 3.3%; *M* (mass spec.), 395.  $C_8F_{15}N$  requires C, 24.3; N, 3.5%; *M*, 395], b.p. 90 °C,  $\lambda_{max}$  (film) 5.91  $\mu m$  (C:N str.).

*Aromatisation of Perfluoro-(2-isopropyl-3,4,5,6-tetrahydropyridine) (7).*—The tetrahydro-compound (2.60 g, 6.58 mmol), contaminated with perfluoro-(2-methylpent-2-ene) (a perfluoropropene dimer also formed in the above reaction) was heated at 300 °C for 24 h in a stainless steel autoclave (16 ml) containing iron filings (*ca.* 2 g). Distillation of the volatile product gave perfluoro-(2-isopropyl-3,4,5,6-tetrahydropyridine) (1.02 g, 39% recovery), b.p. 88–89 °C, and perfluoro-(2-isopropylpyridine) (0.95 g, 2.98 mmol, 80% based on the tetrahydro-compound consumed), b.p. 123 °C, both with the expected i.r. spectra.

<sup>19</sup>F N.m.r. Data.—Chemical shifts were measured for neat liquid samples, using trifluoroacetic acid as an external reference. Relative intensities of signals observed in each case agreed with the structural assignments.

(a) *Mixture (52:48) of perfluoro-(2-methylpentane) (5) and perfluoro-(2,3-dimethylbutane) (6).*

<sup>21</sup> R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Amer. Chem. Soc.*, 1960, **82**, 5831.

<sup>22</sup> R. D. Chambers, W. K. R. Musgrave, and J. Savory, *J. Chem. Soc.*, 1961, 3779.

