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SYNTHESIS OF PERFLUOROCHEMICALS FOR USE AS BLOOD SUBSTITUTES, PART I. ELECTROCHEMICAL FLUORINATION OF N-METHYLDECAHYDROQUINOLINE AND N-METHYLDECAHYDROISOQUINOLINE

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SUMMARY

Electrochemical fluorination of N-methyldecahydroquinoline afforded mainly a mixture of cis and trans N-(F-methyl)-F-decahydroquinoline, their rearranged isomers and F-propyl-F-cyclohexane arising from the cleavage at carbon-nitrogen bonds, in a ratio of approximately 2:4:6:3. N-Methyldecahydroisoquinoline was also fluorinated electrochemically to give a mixture of cis and trans N-(F-methyl)-F-decahydroisoquinoline, their rearranged isomers and 1-(F-ethyl)-2-(F-methyl)-F-cyclohexane in a ratio of approximately 4:4:6:1. No correlation was found between the cis and trans ratio of starting materials and that of the corresponding perfluorinated amines. Fluorination of N-methyl-1,2,3,4-tetrahydroquinoline gave much lower yields.

INTRODUCTION

During the course of our research on a perfluorochemical blood substitute [1a], we found that bicyclic perfluorocarbons such as F-decalin exhibit short body retention but do not make a storable emulsion, whereas perfluorinated acyclic tertiary amines such as tri(F-propyl)amine show the

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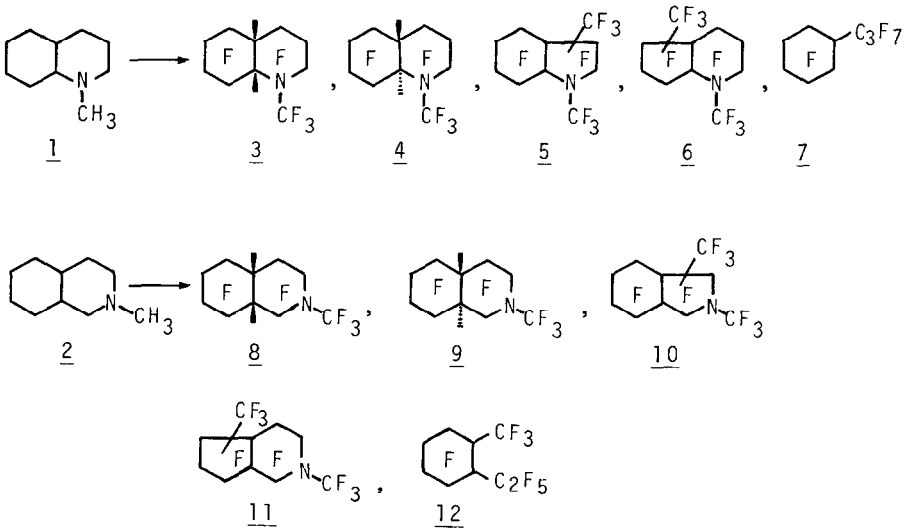
reverse properties: long dwelling time in the body but good emulsion stability [2]. This dilemma has been partly resolved by the combined use of, for example, F-decalin and tri(F-propyl)amine, but the mixed-perfluorochemical emulsion must be frozen to prevent deterioration of the emulsion particles during storage [3]. Under these circumstances, we became interested in the preparation of perfluorinated, bicyclic tertiary amines which might possess the desirable properties of both F-decalin and tri(F-propyl) amine.

The fluorination of quinoline with metal fluoride has been reported [4], but the electrochemical fluorination of fused bicyclic tertiary amines, to the best of our knowledge, has not. We now wish to report the results of the electrochemical fluorination of N-methyldecahydroquinoline and N-methyldecahydroisoquinoline.

RESULTS AND DISCUSSION

Electrochemical fluorination of N-methyldecahydroquinoline (1) and N-methyldecahydroisoquinoline (2) was found to yield mainly a mixture of the corresponding perfluorinated amines, plus isomerized and fragmented products as shown in Scheme 1 and Table 1.



Scheme 1. F in the center of a ring signifies all bonds are to fluorine.

Since the object of this study was to prepare F-tertiary amines close in composition to the expected structures, low-boiling by-products (approximately < 130°) which resulted from fragmentation, usual in electrochemical fluorination, were not investigated. The crude fluorination products were treated with a mixture of 8N potassium hydroxide solution and diisobutylamine to remove products containing residual hydrogen or unsaturation, followed by potassium iodide-acetone solution, to remove nitrogen fluorides. All of these kinds of compounds are thought to be toxic [2] when administered intravenously.

TABLE 1.
Typical electrochemical fluorination of 1 and 2.

Starting material	Passed electricity (Ahr)	Yield (%)[a]		Product distribution (%)[b]
		crude	refined[c]	
1 (0.85 mol)	1056	77	62	3 (9.7), 4 (17.1) 5 and 6 (29.7), 7 (14.7) Others (28.8)[d]
2 (0.85 mol)	1085	65	41	8 (23.8), 9 (21.6) 10 and 11 (31.4) 12 (6.4), Others (16.8)[d]

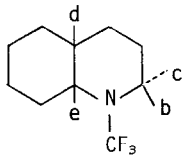
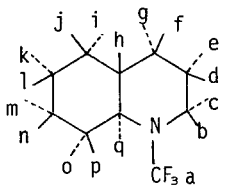
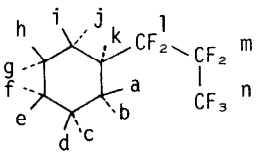
[a] Mol%, based on theoretical amount of the corresponding F-amines.
[b] by g.c.
[c] After treatment with an alkali-amine mixture and KI-acetone solution.
[d] Not identified.

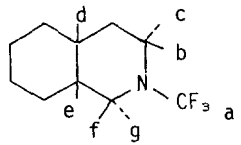
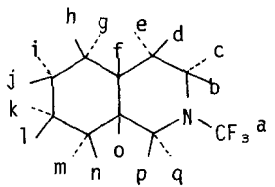
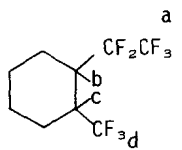
After treatment with the alkali-amine mixture, and KI-acetone solution, the raw perfluorochemical phase was subjected to fractional distillation under reduced pressure through a 120 cm spinning band column. Isolation of each component in the pure state was achieved by preparative-scale g.c. of the appropriate distillation fractions.

The fluorination of 1 gave perfluorochemicals in higher yield than the fluorination of 2, but did not afford the unrearranged bicyclic structures, 3 and 4, in superior formation ratio compared to 2. This was compensated by the isolation of the rearranged products, 5 and 6. The isomers having a five-membered ring were found to form in a similar ratio in both fluorinations. Of particular interest is our observation that there was no correlation between the cis/trans ratio of the starting materials and that of the fluorinated products.

TABLE 2.

^{19}F-nmr spectra of compounds 3, 4, 7, 8, 9 and 12

Compound	Formula[a]	Chemical shift[b,c] and coupling constant[c] (Hz)		
3		a 48.7(3F) b 78.1(ax)] J_{AB}=212 c 101.5(eq)] d 185.1 e 145.5	111.0(ax)] 126.3(eq)] J_{AB} =290 116.8(ax)] 127.7(eq)] J_{AB} =298 121.1(ax)] 133.7(eq)] J_{AB} =298 123.5(ax)] 137.1(eq)] J_{AB} =275 123.5(ax, 2F) 139.7(eq, 2F) J_{AB}=275	
4		a 50.1(3F) b 93.2(eq)] J_{AB}=203 c 84.6(ax)] d 124.6(ax)] J_{AB}=264 e 128.0(eq)] f 137.3(eq)] J_{AB}=271 g 122.6(ax)] h 182.8(1F)	i 119.8] J_{AB}=293 j 130.0] k 141.7] J_{AB}=282 l 122.9] m 121.9] J_{AB}=282 n 139.7] o 130.0] J_{AB}=293 p 115.5] q 134.4(1F)	
7		a(i)118.4(ax)] J_{AB}=300 b(j)129.8(eq)] c(g)122.0(ax)] J_{AB}=286 d(h)139.5(eq)] e 124.1(ax)] J_{AB}=286 f 142.0(eq)]	k 186.0 l 113.2 m 126.1 n 80.5	l-n=14 k-n= 2

8		a 51.3(3F) b 86.0(ax) c 96.2(eq) $]J_{AB}=202$ d,e 182.2(1F) 187.9(1F) f 81.3(ax) g 84.6(eq) $]J_{AB}=210$	121.2(ax) 124.4(eq) $]J_{AB}=295$ 125.5(ax) 132.9(eq) $]J_{AB}=291$ 122.8(2F) 123.7(2F) 130.1(2F)	
9		a 51.6(3F) b 80.5(ax) c 105.8(eq) $]J_{AB}=206$ d 132.4(eq) e 119.9(ax) $]J_{AB}=291$ f,o 180.5(1F) 189.0(1F) g 124.1(ax) h 131.1(eq) $]J_{AB}=285$	i 141.5(eq) $]J_{AB}=275$ j 118.1(ax) k 118.7(ax) $]J_{AB}=275$ l 141.5(eq) m 131.3(eq) $]J_{AB}=285$ n 124.1(ax) p 73.0(ax) $]J_{AB}=209$ q 94.4(eq)	a-b=a-p= 6.5 a-c=a-q=25.3
12		a 81.0 b,c 183.5 d 68.1	140.9	

[a] All unmarked positions are bonds to fluorine.

[b] ϕ value in ppm relative to internal $CFCl_3$. Upfield shifts are quoted as positive.

[c] Only apparent chemical shifts and coupling constant are given.

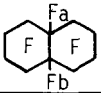
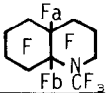
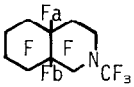
Structure determination of the products was based on spectroscopic data (^{19}F-nmr, GC-MS, and IR). Typical assignments by ^{19}F-nmr for several compounds shown in Scheme 1 are summarized in Table 2.

As these spectra show complicated patterns with many unresolved couplings, only apparent chemical shifts and coupling constants are given. Peak assignments in the spectra of compounds 3, 4, 8 and 9 were done by comparison with the reported spectra of cis and trans F-decalin [5a-c] or N-(F-alkyl)-F-piperidines [6] or N,N-di(F-alkyl)-F-cyclohexylamines [7a-b]. For example, the spectrum of 3 clearly showed the presence of an N-CF_3 group at 48.7 ppm, an AB type quartet of a CF_2 group at 78.1 and 101.5 ppm, and a CF at 145.5 ppm, which are characteristic for fluorines on carbons adjacent to nitrogen. Unassigned signals were observed between 111.0 and 139.7 ppm corresponding to twelve fluorine atoms.

The stereochemistry of compounds 3, 4, 8 and 9 were assigned based on the half-width of signals due to tertiary fluorine atoms. In general, the peak width of tertiary fluorine atom signals of trans isomers is larger than that of the cis, as observed in the F-decadin system [5a], because the tertiary fluorine atoms at the 10-position in the trans-form interacts with three or four fluorine atoms at 1,3-diaxial positions and consequently shows a broader peak. The stereochemistry of 3, 4, 8 and 9 could be thus determined (Table 3).

TABLE 3

Relative half width and chemical shifts of tertiary fluorine atom

Compound[a]		Fa	Fb	Assignment
		1.00 (188.5)[b]	1.00 (188.5)	cis
		1.35 (188.7)	1.35 (188.7)	trans
	3	1.29 (186.4)	2.06 (146.4)	cis
	4	1.94 (182.8)	1.94 (134.4)	trans
	8	0.76 (181.5)	0.76 (180.5)	cis
	9	1.47 (180.5)	1.41 (189.0)	trans

[a] An F symbol within a ring signifies that all unmarked positions in that ring are bonds to fluorine.
[b] Figures in parenthesis indicate chemical shift.

However, as the only exception, half width of Fb in compound 4 does not significantly differ from that of 3, presumably owing to the effect of the neighboring N-CF_3 group.

Infrared spectra of compounds 3, 4, 8 and 9 also gave further support to this stereochemistry; 4 and 9 (trans isomers) show a strong band at 775 cm^{-1}, whereas 3 and 8 (cis isomers) show a much weaker band: 3 and 8, on the other hand, have a stronger band at 860-862 cm^{-1}, while 4 and 9 have only weak bands, as observed in trans and cis decalins [5a, 5d].

Mass spectra of 3 and 4 showed quite simple fragmentation, in which the molecular ion as well as $[M-F]^+$ were clearly observed. Mass spectra of 8 and 9 showed also simple fragmentations and the only significant difference between cis and trans isomers was the abundance of m/e 69 and 113.

The ^{19}F-nmr spectra of 7 and 12 showed the presence of CF_2's with AB quartets, indicating F-cyclohexane structure. The nmr spectrum of 7 is coincident with that of F-propyl-F-cyclohexane reported by Abe et al. [8], while the ^{19}F-nmr spectrum of 12 showed a complicated pattern due to the presence of cis and trans isomers, but clearly indicated the presence of two CF's and F-ethyl and F-methyl groups. Isolation of these isomers by preparative-scale g.c. proved unsuccessful.

The ^{19}F-nmr spectra of 5, 6, 10 and 11 are also very complicated because each of these products consists of two or three isomers. However, each spectrum of 5 and 6, corresponding to either Peak A or B or C in the experimental section, shows an >N-CF_3 group at 48.5-55 ppm and a >CF-CF_3 group at 68.9-75 ppm, with equivalent signal intensities. Two tertiary fluorines were also observed at 174-178 or 174-189 or 171.7-184.8 ppm. Mass spectra of 5 and 6 shows m/e 495$[M]^+$ as well as 426$[M-CF_3]^+$, supporting the proposed structure. Each spectrum of 10 and 11, corresponding to either Peak D or E in the experimental section, also gives typical signals of an >N-CF_3 group at 50-56 ppm and a >CF-CF_3 group at 69-75 ppm, as well as three tertiary fluorines in the region of 178-194 or 179-193 ppm. Their mass spectra exhibit m/e 495$[M]^+$ and/or 476$[M-F]^+$. Proposed structures for 10 and 11 as shown in Scheme 1 may also be supported by the retention time data on g.c.; viz., F-pyrrolidine derivatives exhibit smaller retention time than F-piperidine ones, providing that their molecular weights are the same [9]. (See also experimental section.)

Fluorination of N-methyl-1,2,3,4-tetrahydroquinoline (13) was less successful: the yield of 3 and 4 was as low as ca. 3 mol%, but the product ratio, (3+4)/(5+6), increased three times compared with the fluorination of 1.

EXPERIMENTAL

Fluorination was carried out in the usual way described elsewhere [10] using a 1.5 ℓ electrolytic cell fitted with a reflux condenser (-20°C) on the top of the cell. The effective anodic area was 10.5 dm^2.

Reagents

N-Methyldecahydroquinoline (1) and N-methyldecahydroisoquinoline (2) were derived from quinoline or isoquinoline, respectively, by catalytic hydrogenation [11] followed by methylation under Eschweiler-Clarke reaction conditions: 1, b.p. 102-104°/30 mmHg (lit. [12] 79-81°/10 mmHg), 80-82% yields; 2, b.p. 106-110°/29 mmHg (lit. [12] 75-80°/9 mmHg), 70-75% yields. N-Methyl-1,2,3,4-tetrahydroquinoline (13) was obtained from 1,2,3,4-tetrahydroquinoline (Aldrich, U.S.A.) with dimethyl sulfate: b.p. 121-122°/14 mmHg (lit. [13] 137.5°/30 mmHg), 50-61% yields. Anhydrous hydrogen fluoride (Morita Kagaku Kogyo Co. Ltd.) was more than 99.5% pure.

Spectroscopy

Analytical g.c. work were done with a Shimadzu RIA gas chromatograph using a glass column (3 mm i.d., 6 m long) packed with 5% SE-30 on Chromosorb W for fluorinated products. Preparative-scale g.c. was carried out with a Shimadzu GC-4B gas chromatograph using a copper column (10 mm i.d., 14 m long) packed with 30% SE-30 on Diasolid L-1.

Infrared spectra were recorded on a Shimadzu IR-420 spectrometer. ^{19}F-nmr spectra were recorded on Hitachi R-24F, Varian EM-390 and JEOL JNM-FX 200 spectrometers using CCl_3F as an internal standard, and upfield shifts are quoted as positive. Mass spectra were recorded on a Shimadzu 9020-DF or an LKB-9000 instrument at 70 eV.

Electrochemical fluorination of N-methyldecahydroquinoline (1)

A 130 g portion of 1 was dissolved in about 1.2 ℓ anhydrous hydrogen fluoride in a cell. The electrolysis was then carried out with an initial anodic current density of 2.4-0.3 A/dm^2, a cell temperature of 4-10°, and cell voltage of 5-7 V. The electrolysis was continued until the current reached around 0.1 A at 7 V. The crude products which were drained out were mixed with an equal volume of 8N KOH and diisobutylamine. The mixture was

refluxed for 5 days to remove residual hydrogens and unsaturation, then washed with water, concentrated sulfuric acid, and water in that order and then treated with 3% potassium iodide in aqueous acetone solution to remove compounds having N-F bond(s). The resultant liquid (260 g) was washed with water several times and subjected to fractional distillation under reduced pressure. The individual compounds, which were subsequently characterized spectroscopically, were isolated by preparative-scale g.c. from a portion of the distilled fraction.

cis N-(F-methyl)-F-decahydroquinoline (3): nc, (Found: M 494.9677. $C_{10}F_{19}N$ requires M 494.9729). b.p. 153-155°. IR (film, cm^{-1}): 1380 (m, sh) 1362 (s), 1340 (s, sh), 1318 (s), 1298 (m, sh), 1270 (m), 1240 (s), 1200 (s), 1175 (m, sh), 1162 (m), 1150 (m), 1108 (s), 1065 (s), 1050 (m), 1025 (s), 1005 (mw), 995 (w), 970 (s), 896 (s), 872 (w), 862 (m), 822 (w), 805 (s), 785 (w), 710 (s), 660 (m), 650 (m), 625 (m), 618 (m), 595 (m) cm^{-1}. MS: (given in the following order; mass number, formula, % intensity of base peak): 495[M^+](7.3), 476[M-F](4.4), 388[$C_9F_{14}N$](1.2), 338[$C_8F_{12}N$](1.4), 326[$C_7F_{12}N$](4.7), 295[$C_6F_{11}N$](3.5), 293[C_7F_{11}](1.1), 288[$C_7F_{10}N$](1.4), 276 [$C_6F_{11}N$](2.3), 245[C_5F_9N](4.4), 238[C_6F_8N](7.0), 212[C_5F_8](1.6), 207[C_5F_7N] (1.5), 181[C_4F_7](5.6), 131[C_3F_5](100), 69[CF_3](29.7).

trans N-(F-Methyl)-F-decahydroquinoline (4): nc, (Found: M 494.9763. $C_{10}F_{19}N$ requires M 494.9729). b.p. 154.5-155.5°. IR (film, cm^{-1}): 1355 (s), 1321 (s), 1300 (m, sh), 1275 (s), 1268 (s, sh), 1240 (s, sh), 1215 (s, br.), 1190 (m, sh), 1170 (w), 1150 (s), 1120 (s), 1088 (s), 1070 (m), 1020 (s), 1004 (w), 972 (s), 895 (s), 830 (w), 810 (w), 783 (m, sh), 775 (s), 728 (m), 702 (w), 675 (m), 655 (m), 628 (m), 599 (m), 582 (w).
MS: 495[M^+](5.6), 476 [M-F](3.9), 407[$C_9F_{15}N$](1.1), 388 (1.8), 357[$C_8F_{13}N$](1.4) 338 (2.5), 326 (6.8), 307 [$C_7F_{11}N$](1.9), 295 (4.2), 293 (1.4), 288 (2.3), 243 (2.4), 238 (7.5),212 (2.6), 207 (1.7), 193[C_5F_7](8.5), 131 (100), 69 (46.3).

Analytical g.c. of the bulk of fractions (b.p. 150-155°) showed three components in a ratio of ca. 5:4:2. Each component was isolated by preparative scale g.c. and named as Peak A, B and C according to the order of the elution. Compounds A, B and C were estimated to boil at 150-152°, 151.5-152.5° and 152-154°, respectively, based on the results of spinning-band column distillation. Their respective mass spectra showing m/e 495 [M^+] and ^{19}F-nmr spectra were consistent with the proposed structures 5 or 6 or their stereoisomers, but, we could not ascertain which peak corresponded to which structure.

^{19}F-nmr spectra and mass spectra of A, B and C are given as follows.

Peak A: ^{19}F-nmr: 50-54 (3F,>N-CF_3), 69-75 (3F, ≻CF_3), 75-102 (2F, >NCF_2), 102-140 (9F), 174-178 (2F). MS: 495[M^+](0.5), 476[M-F](16.0), 426[M-CF_3](1.3), 388 (8.3), 326 (3.8), 295 (13.3), 257 (1.5), 245 (2.1), 243 (4.6), 238 (6.0), 231 (1.1), 226 (1.1), 212 (5.3), 181 (30.0), 131 (18.0), 100 (13.3), 69 (100).

Peak B: ^{19}F-nmr: 50-55 (3F, >N-CF_3), 70-73 (3F, ≻CF_3), 72-102 (2F), 102-140 (9F), 174-189 (2F). MS: 495 [M^+](9.0), 476[M-F](7.9), 426[M-CF_3](6.5), 407 (1.4), 388 (4.6), 344 (6.0), 338 (6.3), 326 (8.7), 307 (1.6), 295 (53.1), 293 (1.9), 288 (1.9), 281 (3.5), 276 (5.5), 257 (3.0), 245 (6.3), 243 (6.0), 238 (4.4), 226 (2.5), 212 (7.9), 207 (9.3), 181 (48.8), 150 (5.2), 131 (100), 100 (19.4), 69 (51.0).

Peak C: ^{19}F-nmr: 48.5, 50.8, 51.4, 52.1 (3F, >N-CF_3), 68.9, 71.6 (3F,≻ CF_3) 72.4, 79.0 (J=208 Hz), 83.9 (J=217 Hz), 94.0 (J=217 Hz), 103.0 (J=208 Hz), 110-140 (9F), 171.7, 174.1, 180.3, 184.8 (2F). MS: 495 [M^+](16.4), 476 [M-F] (5.5), 426 [M-CF_3](1.2), 407 (1.9), 395 (9.8), 388 (6.8), 376 (1.8), 345 (2.1), 338 (15.5), 326 (3.6), 307 (3.5), 295 (100), 293 (4.4), 288 (4.4), 281 (1.9), 276 (1.5), 262 (2.2), 257 (9.3), 243 (7.5), 238 (2.6), 212 (17.3), 207 (16.4), 193 (5.7), 181 (59.3), 131 (14.5), 100 (23.6), 69 (92.0).

F-Propyl-F-cyclohexane (7): b.p. 123.5-124.5° (lit. [4a,14] b.p. 124°). IR (film, cm^{-1}): 1350 (s), 1320 (s, br.), 1240 (s, br.), 1205 (s), 1185 (s, sh), 1158 (m, sh), 1138 (m), 1118 (m), 1090 (w), 1055 (w), 1025 (s), 975 (s), 925 (m) 850 (m), 818 (w), 779 (m), 742 (w), 721 (s), 630 (m), 618 (m), 590 (w). MS: 431 [M-F](12.5), 343 [C_8F_{13}](1.1), 331 [C_7F_{13}](24.6), 293 [C_7F_{11}](1.4), 281 [C_6F_{11}](14.6), 262 [C_6F_{10}](1.8), 243 [C_6F_9](8.9), 231 [C_5F_9](16.4), 219 [C_4F_9](1.6), 193 [C_5F_7](5.0), 181 [C_4F_7](28.6), 169 [C_3F_7](71.4), 162 [C_4F_6] (7.9), 131 [C_3F_4](46.0), 119 [C_2F_5](44.6), 100 [C_2F_4](13.9), 93 [C_3F_3](7.5), 69 [CF_3](100).

Electrochemical fluorination of 2

Compound 2 (130 g) was fluorinated similarly under the conditions of 2.3-0.1 A/dm^2; 4-10°; 5-7 V. A mixture of the crude products (172 g) was treated with an alkali-amine mixture and distilled using spinning-band column at 149-154°. The individual compounds were isolated by preparative-scale g.c.

cis N-(F-Methyl)-F-decahydroisoquinoline (8): nc, (Found: M 494.9810. $C_{10}F_{19}N$ requires M 494.9729) b.p. 153-154° IR (film, cm^{-1}): 1342 (s, br.), 1285 (m), 1267 (m, sh), 1240-1210 (s, br.), 1190 (w), 1170 (w), 1152 (w, sh).

1119 (m, sh), 1077 (w), 1060 (mw), 1042 (mw), 1022 (m), 977 (m), 950 (m, sh), 940 (s), 905 (m), 860 (m), 827 (m), 820 (m), 782 (m), 735 (m), 720 (m, sh), 670 (w), 655 (w), 638 (w), 623 (w), 618 (w), 600 (w), 585 (m).
MS: 495 [M^+](1.1), 476 [M-F](22.6), 426 [M-CF_3](3.0), 388 (15.6), 362 [C_8F_{14}] (2.2), 343 (1.5), 338 (1.1), 293 (40.7), 262 (2.6), 250 (1.1), 243 (28.1), 212 (1.5), 205 (2.6), 202 [C_3F_8N](2.2), 193 (8.1), 131 (68.1), 114 [C_2F_4N](12.2) 100 (44.4), 93 (5.2), 69 (100).

trans N-(F-Methyl)-F-decahydroisoquinoline (9), nc (Found: M 494.9741. $C_{10}F_{19}N$ requires M 494.9729) b.p. 153-154° IR (film, cm^{-1}): 1362 (m, sh), 1343 (s, br.), 1330 (m, sh), 1290 (s), 1261 (s), 1230-1210 (s, br.), 1187 (w), 1155 (w), 1130 (w, sh), 1120 (m), 1061 (s), 1038 (s), 1005 (m), 991 (m), 975 (w), 940 (m, sh), 930 (s), 902 (m), 860 (w), 850 (w), 825 (w), 818 (w), 803 (w), 790 (m, sh), 775 (s), 720 (m), 679 (m), 643 (m), 635 (w), 600 (m).
MS: 495 [M^+](2.3), 476 [M-F](24.8), 426 [M-CF_3](1.6), 388 (17.4), 362 (1.3), 343 (1.3), 293 (38.7), 262 (1.6), 255 (1.0), 243 (16.1), 212 (1.3), 205 (1.9), 202 (2.9), 193 (5.2), 131 (100), 114 (10.0), 100 (29.7), 69 (80.6).

A fraction boiling at 149-153° was shown by analytical g.c. to consist of two major components (compound D and E, named according to the order of elution), subsequently identified as 10 and 11 or vice versa, by ^{19}F-nmr. Compound D and E were estimated to boil at 149-151° and 151-153° respectively, from the results of spinning-band column distillation. Though the products were not completely separable by preparative-scale g.c., compound D could be assigned to 10, and E to 11 by ^{19}F-nmr, mass spectra and g.c. [9], which are shown as follows.

Peak D (10): nc, b.p. 149-151° (estimated), ^{19}F-nmr: 50-53 (3F, >NCF_3), 69-75 (3F, ≻CF_3), 75-108 (4F), 110-140 (6F), 179-193 (3F).
MS: 495 [M^+](0.4), 476 [M-F](19.1), 426 [M-CF_3](10.9), 388 (12.3), 343 (1.3), 338 (2.1), 300 [C_6F_{12}](1.3), 293 (42.6), 288 (1.1), 274 [C_7F_{10}](2.8), 250 [C_5F_{10}](1.5), 243 (9.4), 231 (1.5), 212 (3.8), 205 [C_6F_7](4.0), 202 (4.7), 193 (24.5), 181 (11.7), 131 (29.1), 114 (10.4), 100 (23.4), 69 (100).

Peak E (11): nc, b.p. 151-153° (estimated). ^{19}F-nmr: 50-56 (3F, >NCF_3), 69-74 (3F, ≻CF_3), 74-108 (4F), 110-140 (6F), 178-194 (3F).
MS: 476 [M-F](30.0), 426 [M-CF_3](3.7), 388 (17.0), 362 (5.0), 343 (3.7), 338 (1.3), 300 (1.7), 293 (45.0), 274 (3.7), 262 (2.0), 255 (1.0), 250 (2.0), 243 (3.7), 212 (3.7), 205 (4.0), 202 (3.7), 200 (1.0), 181 (27.3), 131 (50.0), 114 (13.3), 100 (23.3), 69 (100).

1-(F-Ethyl)-2-(F-methyl)-F-cyclohexane (12): nc, b.p. 128-130°, IR (film, cm^{-1}):1330 (s), 1260-1230 (s, br.), 1200 (s), 1130 (w), 1113 (m),

1073 (m), 1045 (m), 1018 (m), 998 (m), 988 (w, sh), 975 (m), 958 (w), 925 (m), 902 (w), 870 (m), 865 (m), 839 (w), 800 (m), 746 (m), 735 (ms), 725 (m, sh), 710 (w, sh),690 (w, sh), 675 (mw), 660 (w, sh), 640 (w), 625 (w, sh), 618 (w). MS: 431 [M-F](1.4), 381 [C_8F_{15}](2.0), 343 [C_8F_{13}](2.0), 331 [C_7F_{13}](2.4), 293 [C_7F_{11}](5.3), 243 [C_6F_9](9.6), 231 [C_5F_9](10.8), 212 (3.7), 205 (1.0), 181 (15.7), 169 (5.3), 131 (22.9), 119 (69.9), 100 (7.8), 69 (100).

Fluorination of N-methyl-1,2,3,4-tetrahydroquinoline (13)

Compound 13 (58 g) was fluorinated similarly to give a large amount of tarry material and about 10 g of a perfluorochemical mixture. The resultant liquid was shown by analytical g.c. to consist of 3 (21%), 4 (30%), compound A (9%), B (8%), C (2%), 7 (8%) and others (22%).

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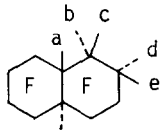
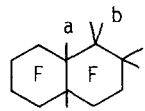


a 188.7
b 131.7] 299 Hz
c 124.7]
d 120.3] 30 Hz
e 142.2] 281 Hz



a 188.5
b ~125
c ~135

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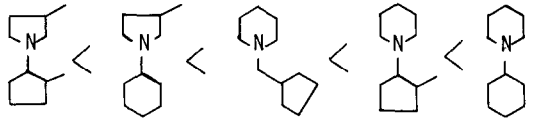

All unmarked bonds are to fluorine unless otherwise described.

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