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POLYHALOGENOHETEROCYCLIC COMPOUNDS. PART 37 [1]. PERFLUOROTETRAHYDRO-QUINOLINE, -ISOQUINOLINE, AND RELATED COMPOUNDS

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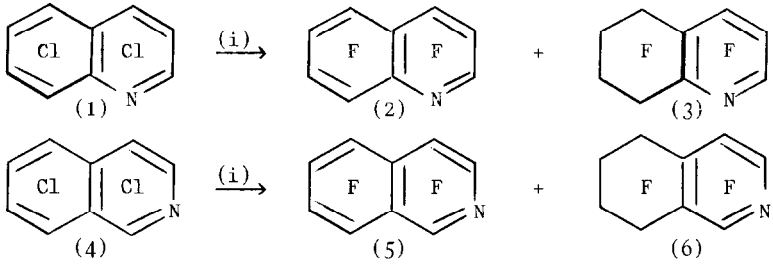
SUMMARY

The formation of perfluorotetrahydro-quinoline (3) and -isoquinoline (6) in the high temperature reaction between KF and heptachloro-quinoline and -isoquinoline is investigated and a mechanism is proposed. Compounds (3) and (6) represent unusually substituted pyridine derivatives and the orientation of substitution in reactions with nucleophiles is reported.

RESULTS AND DISCUSSION

Some years ago we reported the syntheses of perfluoro-quinoline and -isoquinoline [2] and, in the course of subsequent preparations, noted the accompanying formation of perfluorotetrahydro-quinoline (3) and -isoquinoline (6) during reactions of the corresponding perchloro derivatives (1) and (4) with potassium fluoride at elevated temperatures, using autoclaves. The production of (3) and (6) was especially noticeable as temperatures significantly exceeded those reported for the formation of perfluoro-quinoline and -isoquinoline (2) and (5) [2].



(i) KF, autoclave, elevated temperatures.

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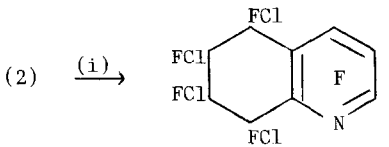
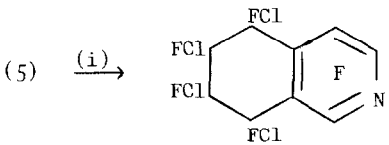
In the intervening period, Sartori and co-workers have also observed and reported on the formation of (3) and (6), in repeating our procedures [3,4]. We have been puzzled about the formation of (3) and (6), i.e. formally an addition of fluorine via fluoride ion and here we report experiments that cast some light on a possible process.

Since the formation of (3) and (6) is more effective as the temperatures become more severe it seems reasonable to conclude that the fundamental step involves decomposition of (1) and (4) to give elemental chlorine, which then adds to fluorinated or partly fluorinated quinolines or isoquinolines, as they are formed. Consequently, we have now made chlorofluoro derivatives (7) and (8) by ultraviolet initiated addition of chlorine to perfluoro-quinoline (2) and -isoquinoline (5) respectively. In both cases, a product approximating to $C_9F_7Cl_4N$ was obtained and, in the case of the quinoline system, a good yield of (7) was obtained. The situation with (5) was,



(7) (87%)



(8)

(i) Cl_2, u.v. (ii) KF, various conditions. (iii) CsF, sulpholan.

however, more complicated and the complexity of the F-19 n.m.r. spectrum indicated that some addition to the pyridine ring may also have occurred.

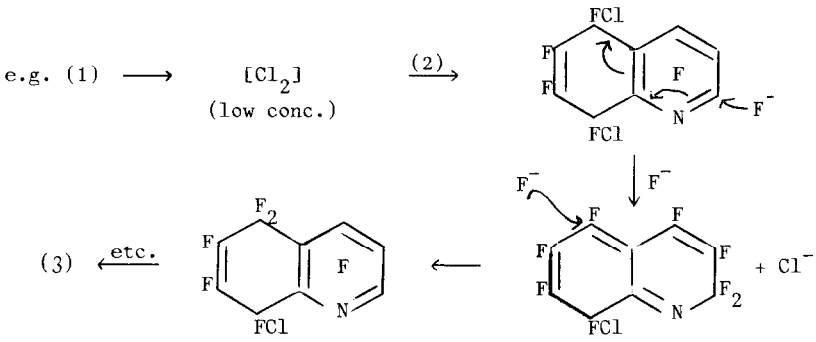
We have studied reactions of (7) and the corresponding product mixture (8), with potassium fluoride under a variety of conditions and, in both cases, the corresponding perfluorotetrahydro derivatives i.e. (3) and (6) were obtained. Surprisingly, the chlorination product (8), which is probably a mixture of isomers, gave the best yields of perfluorotetrahydro-derivative (6).

The results shown in Table 1 demonstrate the fact that chlorine in the carbocyclic rings in (7) and (8) may be exchanged extensively for fluorine using alkali-metal fluorides and this provides a basis for understanding the

TABLE 1

	Conditions	% Yields of (3) & (6)	
(7)	KF, Autoclave, 400°C	(3)	(15%)
	x.s. CsF, Sulpholan, 160°C	(3)	(10%)
	CsF, Sulpholan, 155°C	(3)	(8%)
		+ $C_9F_{10}NCl$	(36%)
(8)	x.s. CsF, Sulpholan, 160°C	(6)	(21%)
	CsF, Sulpholan, 160°C	(6)	(33%)

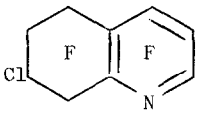
formation of (3) and (6) from (1) and (4) respectively, in reactions with potassium fluoride under extreme conditions. Thus it has been demonstrated that a net addition of fluorine to an aromatic system can occur via initial addition of chlorine followed by fluoride ion displacement. It is clear, however, that the tetrachloro derivatives are not, themselves, formed under severe conditions since no significant quantities of (3) and (6) were formed from (7) and (8) with potassium fluoride in an autoclave at temperatures greater than 400°C. It is likely, therefore, that the slow decomposition of (1) or (4) under severe conditions produces small equilibrium concentrations of chlorine in the autoclave, which add to (2) or (5) and lead to rapid replacement by fluorine, under these conditions.



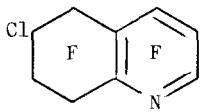
Scheme 1

The reaction of (8) with caesium fluoride in a solvent gave a surprisingly high yield of (6) (33%) and this shows that the type of reaction which involves addition of fluoride ion to the heterocyclic ring, accompanied by displacement of chloride from the carbocyclic ring, can occur very extensively. The analogous reaction with (7), however, led to a

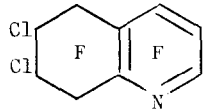
mono-chloro compound as the principal product, whose structure is ambiguous but the chlorine atom most likely remains in one of the ß-positions of the carbocyclic ring (9a, 9b). Yakobson and co-workers [5] have noted that displacement of chlorine is more difficult from the ß-positions in chlorofluorotetralins, in similar reactions involving caesium fluoride. A dichloro derivative, probably (10) is also obtained under different conditions. Thus, the isolation of these partly chlorinated materials from the reaction of (7) with fluoride ion at least supports the overall concept of net addition of fluorine being possible by addition of chlorine followed by successive fluoride ion displacements. Beyond this it is, of course, impossible to reproduce stepwise the process outlined in Scheme 1 because the actual reaction conditions are very severe and only small concentrations of chlorine will be produced. Consequently, addition and displacement will probably occur very quickly.



(9a)



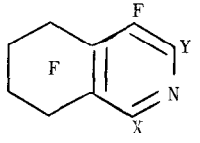
(9b)



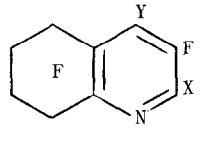
(10)

Further fluorination of fluorinated heterocyclic compounds, using cobal trifluoride, has been carried out successfully in these laboratories [7,8] and the formation of (3) and (6) occurs in passing (2) or (5) over cobalt trifluoride (see experimental section). Compound (3) is also obtained in the fluorination of quinoline by cobalt trifluoride [6].

The perfluorotetrahydro derivatives (3) and (6) are, in effect, fluorinated pyridine derivatives with unusual substitution patterns and, consequently, orientation of nucleophilic substitution is of interest. The isoquinoline derivative (6) reacted with methoxide in methanol giving (11a) as the exclusive mono-substitution product and (11b) as the di-substituted derivative. Likewise, (11c) was formed from diethylamine. A mixture of monomethylethers (12a, 25%) and (12b, 75%) or a dimethylether



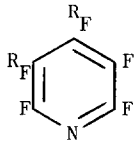
(11a, X = F; Y = OMe)
(11b, X = Y = OMe)
(11c, X = F; Y = NEt_2)



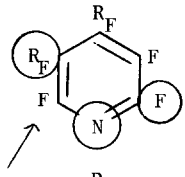
(12a, X = F; Y = OMe)
(12b, X = OMe; Y = F)
(12c, X = Y = OMe)
(12d, X = NH_2; Y = F)
(12e, X = F; Y = NH_2)

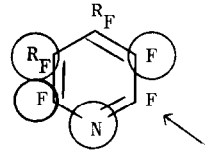
(12c) was obtained from (3) with methoxide in methanol, while ammonia gave an equimolar mixture of (12d) and (12e).

These orientations for nucleophilic substitution are those anticipated from using the now well-established facts that ring-nitrogen is the dominant activating influence at ortho- and para-positions; perfluoroalkyl is strongly activating at ortho- and para-positions; and fluorine atoms ortho- and meta- to the site of nucleophilic attack are activating, while the effect of a para-fluorine atom may be largely ignored [9]. For example, (6) may be regarded as a perfluorodialkylpyridine and, comparing 2-attack and 6-attack by a nucleophile, it is clear that there are more groups at the most favourable activating positions for 6-attack than 2-attack. Using the same type of argument for (3) we conclude that there is no obvious difference in activating effects of groups for 4- and 2-attack. This is borne out by the similar amounts of amino derivatives (12d,e) formed and the fact that

(6) ≡ 

(R_F = polyfluoroalkyl)

2-Attack 

6-Attack 

both monomethylethers (12a,b) are formed albeit with a preference for (12b).

EXPERIMENTAL

^{19}F n.m.r. spectra were recorded using a Varian A56/60D or EM360L, or a Bruker HX90E spectrometer, with $CFCl_3$ and TMS as external references. Upfield shifts are quoted as positive. Mass spectra were recorded on a V.G. Micromass 12B linked with g.l.c. G.l.c. was carried out using a Varian Aerograph instrument fitted with a gas density balance detector and columns packed with 20% 'Krytox'* on Chromosorb W (Column K) or 30% silicone-gum rubber SE-30 on Chromosorb P (Column O). Percentage yields quoted were measured either by weighing products or by g.l.c. analysis using a gas density balance detector. Cobalt trifluoride fluorinations were carried out, as previously described [7], in a reactor of

*E.I. du Pont de Nemours Ltd. registered trade mark.

conventional design. Caesium fluoride doped with sulpholan was prepared by placing dry caesium fluoride (10 g) and dry sulpholan (20 ml) in one arm of a dry Schlenk tube which was purged with nitrogen. These reagents were stirred together and then filtered through the sinter, and more sulpholan was removed by heating under vacuum to give caesium fluoride doped with sulpholan.

Chlorination of heptafluoroquinoline (2)

Chlorine (1 l, 44.6 mmol) and sublimed (2) (5.0 g, 19.6 mmol), contained in a sealed evacuated Carius tube, were irradiated for 24 h by a 1 kW high pressure mercury lamp. The tube was then frozen in liquid air, opened, and the viscous oil washed out with dry ether (150 ml). The ether was washed with water (2 x 25 ml), dried, and evaporated under reduced pressure leaving an oil that was then transferred under high vacuum (100°C, 0.001 mm Hg), to give 5,6,7,8-tetrachloroheptafluoroquinoline (7) (nc) (6.8 g, 87%) b.p. > 200°C. Analysis: Found: C, 27.3; Cl, 36.2; F, 33.9; N, 3.7%; M^+, 395 (for 4 x ^{35}Cl). $C_9Cl_4F_7N$ requires C, 27.2; Cl, 35.8; F, 33.5; N, 3.53%; M, 395 (for 4 x ^{35}Cl); δ_F 75.2 (m, 2-F), 85.5-101 (2F, 2CFCl's), 109-125.5 (3F, 2CFCl's and 4-F), and 156.2 (m, 3-F).

Reaction of 5,6,7,8-tetrachloroheptafluoroquinoline (7) with fluoride ion

(a) At 400°C

Compound (7) (5.1 g, 12.8 mmol) and potassium fluoride (10 g, 170 mmol) were sealed into an evacuated nickel lined autoclave (150 ml) and heated to 400°C for 3 h. The autoclave was vented into a trap cooled in liquid air and analysis of the product (2.5 g) by g.l.c. (Column O; 250°C) showed it to be largely heptafluoroquinoline (2) but also contained some material (ca. 15%) of the same retention time as perfluoro-5,6,7,8-tetrahydroquinoline (3).

(b) At 155°C

A mixture containing compound (7) (3.3 g, 8.3 mmol), caesium fluoride (9.6 g, 63.2 mmol), and sulpholan (15 ml) was stirred at 155°C for 26 h under dry nitrogen. Transference under vacuum gave a colourless liquid (1.27 g) which was shown by g.l.c. (Column K; 170°C) to be a mixture of two components. The more volatile component was identified as (3) (8%) by

comparison of g.l.c. retention time and m.s. breakdown pattern with those of a known sample [10]. The less volatile component was identified as $C_9F_{10}NCl$ (36%) by mass spectroscopy. Preparative scale g.l.c. isolated 6 (or 7)-chloroperfluoro-5,6,7,8-tetrahydroquinoline (9) (nc). Analysis: Found: C, 31.2; N, 4.3%; M^+, 347 (for ^{35}Cl). $C_9ClF_{10}N$ requires C, 31.08; N, 4.03%; M, 347 (for ^{35}Cl); δ_F 70.92 (1F, m, 2-F), 87.05 and 117.88 (2F, AB, J 293 Hz, 5 or 8-CF_2), 99.92 and 110.56 (2F, AB, J 293 Hz, 8 or 5-CF_2), 116.25 (1F, m, 4-F), 119.15 and 134.15 (2F, AB, J 293 Hz, 6 or 7-CF_2), 134.24 (1F, m, CFCl), and 153.15 (1F, m, 3-F).

A similar reaction was carried out using (7) (4.5 g, 11.3 mmol), caesium fluoride (7.4 g, 48.7 mmol) and sulpholan (15 ml). Work-up gave a liquid (1.71 g) and m.s.-g.l.c. (Column K; 175°C) indicated the presence of (9) (12%) and $C_9Cl_2F_9N$ (35%). Separation by preparative scale g.l.c. (Column K) gave (10); Analysis; Found: C, 30.1; N, 4.1%; M^+, 363 (for ^{35}Cl). $C_9Cl_2F_9N$ requires C, 29.75; N, 3.86%; M, 363 (for ^{35}Cl). The ^{19}F n.m.r. spectrum was complex but contained resonances at 73.3, 123.4, and 155.1 attributable to the 2-, 3-, and 4-F of the heteroaromatic ring.

(c) At 160°C

A mixture containing compound (7) (3.5 g, 8.9 mmol) and caesium fluoride doped with sulpholan (10 g, ca. 65 mmol) was stirred at 160°C for 24 h under dry nitrogen. After cooling, the residue was mixed with water (200 ml) and chloroform (200 ml), and the chloroform layer was separated. The aqueous layer was re-extracted with chloroform (2 x 100 ml) and the combined chloroform layers were washed with water (3 x 200 ml). After drying ($MgSO_4$) and filtering, the solvent was removed to leave a brown oil from which (3) (0.3 g, 10%), identified by comparison of i.r. spectra, was obtained by transference under vacuum [10].

Chlorination of heptafluoroisoquinoline (5)

Chlorine (1 l, 44.7 mmol) and sublimed (5) (5.0 g, 19.6 mmol), contained in a sealed evacuated Carius tube, were irradiated for 96 h by a 500 W medium pressure mercury lamp. Following the work-up procedure given for the chlorination of (2) an oil was isolated. Transference under vacuum (100°C, 0.005 mm Hg) gave 5,6,7,8-tetrachloroheptafluoroisoquinoline (8) (nc) (4.6 g, 60%) b.p. > 200°C. Analysis: Found: C, 28.0; F, 33.0%; M^+, 395 (for 4 x ^{35}Cl). $C_9Cl_4F_7N$ requires C, 27.2; F, 33.5%; M, 395 (for 4 x ^{35}Cl); δ_F

60.7 (1F, m, 1-F), 79.7 (1F, m, 3-F), 94.0 (1F, m, CFCl), 106.2 (2F, m, 2CFCl's), and 142.4 (2F, m, 4-F and CFCl).

Subsequent experiments found 5,6,7,8-tetrachloroheptafluoroisoquinoline as the principal component (ca. 70%) of mixture of chlorinated products.

Reaction of '5,6,7,8-tetrachloroheptafluoroisoquinoline' (8) with fluoride ion

(a) At 160°C with caesium fluoride

A mixture containing (8) (4.0 g), caesium fluoride (9.1 g, 5.9 mmol), and sulpholan (10 ml) was stirred at 160°C for 24 h. Transference under vacuum gave a colourless liquid which was identified as compound (6) (1.1 g, 33%) by comparison of g.l.c. retention time and i.r. spectrum with those of a known sample [11].

(b) At 160°C using caesium fluoride doped with sulpholan

A mixture containing compound (8) (4.0 g, 10.1 mmol) and caesium fluoride doped with sulpholan (10 g, ca. 65 mmol) was stirred at 160°C for 24 h under dry nitrogen. After cooling, the mixture was added to chloroform (200 ml) and water (200 ml). The aqueous layer was extracted further with chloroform (2 x 100 ml) and the combined chloroform extracts were washed with water (3 x 200 ml). After drying ($MgSO_4$) and filtering, the solvent was removed to leave a brown oil which was shown by g.l.c. (Column O; 150°C) to consist essentially of two components. These were separated by preparative scale-g.l.c. and the more volatile component was identified as (6) (0.7 g, 21%) by comparison of its i.r. spectrum with that of a known sample [11].

Fluorination of heptafluoroquinoline using CoF_3

Heptafluoroquinoline (2) (16.0 g, 63 mmol) was heated at 180-190°C and carried into the reactor (150-160°C) in a stream of nitrogen. The product mixture was found to contain perfluorotetrahydroquinoline (3) (80% of mixture) by m.s.-g.l.c., together with more highly fluorinated material.

Fluorination of heptafluoroisoquinoline using CoF_3

Heptafluoroisoquinoline (5) (4.0 g, 16 mmol) was heated at 150-160°C and carried into the reactor (120-130°C) in a stream of nitrogen. The

product mixture (2.4 g) was found to contain perfluorotetrahydroisoquinoline (6) (15% of mixture) by m.s.-g.l.c., together with a mixture of perfluorodihydroisoquinolines and more highly fluorinated material (45% of mixture).

Reactions of perfluoro-5,6,7,8-tetrahydroisoquinoline (6)

(a) With one equivalent of sodium methoxide

Compound (6) (1.0 g, 3.02 mmol) was stirred with dry methanol (30 ml) and sodium (0.07 g, 3.04 mmol) was added. Stirring was continued at room temperature for 2 h. The methanol was then removed and the residue was mixed with water (50 ml) and cyclohexane (50 ml). The organic layer was separated and dried ($MgSO_4$). After filtering, the solvent was removed from the filtrate and the resulting yellow solid was sublimed (0.005 mm Hg, 70°C) to give white 3-methoxy-perfluoro-5,6,7,8-tetrahydroisoquinoline (11a) (nc) (0.65 g, 63%), m.p. 42-43°C. Analysis: Found: C, 35.1; H, 1.3%; M^+, 343. $C_{10}H_3F_{10}NO$ requires C, 35.00; H, 0.88%; M, 343; δ_F (acetone) 69.3 (1F, dt, J 29 and 18 Hz, 1-F), 107.6 (2F, brd, J 18 Hz, 8-CF_2), 110.8 (2F, brd, J 18 Hz, 5-CF_2), 137.3 (3F, br, 6-CF_2 and 7-F), and 144.6 (1F, dt, J 29 and 18 Hz, 4-F); δ_H 3.8 (OCH_3).

(b) With two equivalents of sodium methoxide

Compound (6) (1.00 g, 3.02 mmol) was stirred with dry methanol (30 ml) and sodium (0.15 g, 6.53 mmol) was added. The resulting mixture was refluxed for 18 h after which a similar work-up to that in (a) gave a yellow solid, which was shown by g.l.c. (Column O; 240°C) to be a mixture of two components. The most volatile, minor, component had the same retention time as (6). The major component was separated by preparative scale g.l.c. (Column O; 250°C) to give white 1,3-dimethoxyperfluoro-5,6,7,8-tetrahydroisoquinoline (11b) (nc) (0.35 g, 33%), m.p. 56-57°C. Analysis: Found: C, 37.2; H, 1.5; N, 4.3%; M^+, 355. $C_{11}H_6F_9NO_2$ requires C, 37.20; H, 1.70; N, 3.94%; M, 355; δ_F (Acetone) 109.2 (2F, brs, 8-CF_2), 110.4 (2F, brd, J 19 Hz, 5-CF_2), 136.8 (4F, brs, 6- and 7-CF_2), and 153.9 (1F, t, J 19 Hz, 4-F); δ_H (CCl_4) 3.8 (OCH_3).

(c) With diethylamine

A mixture containing compound (6) (2.00 g, 6.04 mmol), ethanol (30 ml), and diethylamine (0.44 g, 6.03 mmol) was stirred at room temperature for 18 h. Following a similar work-up procedure to that in (a) a yellow oil was

obtained. This was sublimed at (0.005 mm Hg, 70°C) and g.l.c. (Column O; 250°C) showed that two components were present in the resulting material. Preparative scale g.l.c. gave 3-diethylaminoperfluoro-5,6,7,8-tetrahydroisoquinoline (11c) (nc) as a yellow liquid (0.46 g, 20%), b.p. > 200°C. Analysis: Found: C, 40.2; N, 6.8%; M^+, 384. $C_{13}H_{10}F_{10}N_2$ requires C, 40.64; N, 7.29%; M, 384; δ_F 66.2 (1F, dt, J 28 and 18 Hz, 1-F), 105.5 (2F, brd, J 18 Hz, 8-CF_2), 110.9 (2F, brd, J 18 Hz, 5-CF_2), 136 (4F, brs, 6- and 7-CF_2), and 143.2 (1F, t, J 19 Hz, 4-F); δ_H 1.2 (3H, t, J 7 Hz, CH_3) and 3.5 (2H, q, J 7 Hz, CH_2).

Reactions of perfluoro-5,6,7,8-tetrahydroquinoline (3)

(a) With one equivalent of sodium methoxide

Compound (3) (5.0 g, 15.1 mmol) was dissolved in dry methanol (30 ml). Sodium methoxide (15 ml of a 1.0 M solution in methanol) was added slowly at room temperature over a period of 5 min. The solution was stirred for a further 5 min., then poured into water (100 ml). The aqueous mixture was acidified (dil. HCl) and extracted with ether (3 x 50 ml). The combined extracts were dried and evaporated under reduced pressure to leave a clear liquid (4.9 g, ca. 95%). G.l.c. (Column O; 150°C) showed it to be a mixture containing mainly (> 85%) two isomeric monomethylether derivatives (2.3:1), together with a dimethylether derivative and starting material as minor components. Separation by preparative scale g.l.c. (Column O; 120°C) gave the major and more volatile component 2-methoxyperfluoro-5,6,7,8-tetrahydroquinoline (12a) (nc), m.p. ca. 18°C, b.p. 168°C. Analysis: Found: C, 35.3; H, 0.9; F, 55.1; N, 3.9%; M^+, 343. $C_{10}H_3F_{10}NO$ requires C, 34.98; H, 0.87; F, 55.39; N, 4.08%; M, 343; δ_F 107.2 (2F, CF_2), 112.3 (2F, CF_2), 127.3 (1F, dt, J 15.5 and 16.5 Hz, 4-F), 135.2 (2F, CF_2), 136.1 (2F, CF_2), and 157.6 (1F, dt, J 15.5 and 3 Hz, 3-F); δ_H 3.94 (OCH_3). The second component was identified as 4-methoxyperfluoro-5,6,7,8-tetrahydroquinoline (12b) (nc), b.p. 193°C. Analysis: Found: C, 34.7; H, 1.0; F, 55.0; N, 3.8%; M^+, 343. $C_{10}H_3F_{10}NO$ requires C, 34.98; H, 0.87; F, 55.39; N, 4.08%; M, 343; δ_F 80.0 (1F, d, J 23 Hz, 2-F), 111.4 (2F, CF_2), 113.9 (2F, CF_2), 136.7 (2F, CF_2), 138.1 (2F, CF_2), and 155.9 (1F, d, J 23 Hz, 3-F); δ_H 4.1 (OCH_3).

(b) With two equivalents of sodium methoxide

Sodium methoxide (6.1 ml of a 1.0 M solution in methanol) was slowly added to a stirred solution of compound (3) (1.0 g, 3.0 mmol) in methanol (20 ml) at room temperature under an atmosphere of dry nitrogen. After stirring for 15 min the solution was poured into water (100 ml). Following the work-up procedure as in (a) a white solid (1.5 g) was obtained. The solid was recrystallized from methanol to give 2,4-dimethoxyperfluoro-5,6-7,8-tetrahydroquinoline (12c) (nc) (70%), m.p. 48°C. Analysis: Found: C, 36.9; H, 2.0; F, 47.9; N, 3.9%; M^+, 355. $C_{11}H_6F_9NO_2$ requires C, 37.18; H, 1.69; F, 48.16; N, 3.94%; M, 355; δ_F (d_6-acetone) 106.3 (2F, CF_2), 111.8 (2F, CF_2), 134.0 (2F, CF_2), 135.2 (2F, CF_2), and 153.8 (1F, t, J 4 Hz, 3-F); δ_H 3.9 (3H, s, 2-OCH_3) and 4.0 (3H, d, J 4 Hz, 4-OCH_3).

(c) With ammonia

Compound (3) (3.3 g, 10 mmol) was dissolved in acetone (30 ml). Ammonia (1.7 ml of 0.880 g ml^{-1}, 31.4 mmol) was dissolved in acetone (10 ml) and slowly added to the stirred solution of the substrate over 5 min. The solution was stirred for 0.5 h, then poured into water (100 ml). The aqueous suspension was extracted with ether (3 x 50 ml), the combined extracts dried and evaporated under reduced pressure. G.l.c. (Column O; 120°C) showed the product (3.2 g, 97%) to be a mixture of two components. The components were separated by preparative scale g.l.c. (Column O; 125-140°C) and gave, after recrystallization from petroleum ether (b.p. 60-80°C), 4-aminoperfluoro-5,6,7,8-tetrahydroquinoline (12e) (nc), m.p. 124°C. Analysis: Found: C, 32.6; H, 0.6; F, 57.4; N, 8.3%; M^+, 328. $C_9H_2F_{10}N_2$ requires C, 32.93; H, 0.61; F, 57.93; N, 8.54%; M, 328; δ_F (d_6-acetone) 86.6 (1F, d, J 23 Hz, 2-F), 109.9 (2F, CF_2), 111.7 (2F, CF_2), 135.1 (2F, CF_2), 136.2 (2F, CF_2), and 161.2 (1F, d, J 23 Hz, 3-F); δ_H 6.3 (brs, 4-NH_2). The less volatile component was similarly separated and recrystallized, and identified as 2-aminoperfluoro-5,6,7,8-tetrahydroquinoline (12d) (nc), m.p. 111°C. Analysis: Found: C, 33.0; H, 0.8; F, 57.3; N, 8.4%; M^+, 328. $C_9H_2F_{10}N_2$ requires C, 32.93; H, 0.61; F, 57.93; N, 8.54%; M, 328; δ_F (d_6-acetone) 105.1 (2F, CF_2), 112.4 (2F, CF_2), 132.2 (1F, dt, J 16 and ca. 16 Hz, 4-F), 134.9 (2F, CF_2), 135.6 (2F, CF_2) and 160.0 (1F, d, J 16 Hz, 3-F); δ_H 6.8 (br, 2-NH_2).

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