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FLUORINATIONS WITH COMPLEX METAL FLUORIDES PART 8. RING REARRANGEMENT IN THE FLUORINATIONS OF QUINOLINE WITH CAESIUM TETRAFLUOROCOBALTATE AND WITH COBALT(III) FLUORIDE*

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SUMMARY

Fluorination of quinoline by caesium tetrafluorocobaltate at ca. 350° afforded mainly a mixture of pentadecafluoro-2-azabicyclo[4,4,0]dec-1(2)-ene (E), and heptadecafluoro-1-azabicyclo[5,3,0]decane (F), arising by skeletal rearrangement. Minor products were six polyfluorocyclohexa[b]-pyridines (G-L) all with carbocyclic rings having the $-(CF_2)_4-$ moiety. Compound F was unreactive, but E was highly susceptible to nucleophiles, e.g. water and methanol. Isoquinoline was fluorinated similarly, but the only new product isolated was tridecafluoro-3-azabicyclo[4,4,0]deca-1(6)-2-diene (R). The rearrangement occurring with quinoline prompted a re-examination of its fluorination by cobalt(III) fluoride. At ca. 350°, compound F was the major product, with very little E: there were some ring-opened materials, the most important being tetradecafluoro-4-pentafluoroethyl-2-azaoct-2(Z)-ene (N).

INTRODUCTION

Part 7 of this series [1] described fluorination of the three picolines by caesium tetrafluorocobaltate [2], which gives the highest proportions of arene-type fluorocarbon products from aromatic precursors, including some hexa- and pentafluorobenzene from benzene. Naphthalene or tetralin gave some perfluorotetralin [3], whilst pyridine afforded pentafluoro- and

* This type of fluorination is the subject of a provisional patent application.

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2,3,4,5-tetrafluoropyridine and perfluoro-N-methylpyrrolidine [4; 5]. It was therefore of interest to fluorinate quinoline over caesium tetrafluorocobaltate; if aromatic products were formed, what structures had they?

Few other fluorinations of pyridine-based heterocycles by high-valency metallic fluorides (HVMFs) have been reported. Pyridine itself with cobalt(III) fluoride at 350° gave fragmentation products and a little undecafluoropiperidine, 2,6-dimethylpyridine giving an analogous result [6]. Pyridine and 4-methylpyridine with potassium tetrafluorocobaltate at 200-230° gave largely ring-opened products [7], but some polyfluoropyridines were also formed [8]. With pyridine there was also some rearrangement to give polyfluoro-N-methylpyrrolidines [7,8], as there was with the picolines and $CsCoF_4$ [1].

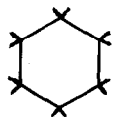
There is one early report [9] of a fluorination of quinoline by an HVMF; cobalt(III) fluoride at 400° gave a product from which, after treatment with ethanol and uranium (VI) hexafluoride, there was isolated perfluoro-n-propylcyclohexane and a saturated heterocycle, $C_9F_{17}N$, thought to be heptadecafluorodecahydroquinoline (P; see Scheme).

RESULTS AND DISCUSSION

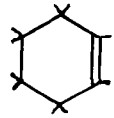
Quinoline passed over caesium tetrafluorocobaltate in a stirred reactor at 335-350° underwent a smooth fluorination to give a good recovery of product (twice the weight of starting material) but this was a complex mixture. Rough separation by distillation, followed by involved glc separations, gave the principal constituents (Table 1 and Scheme). There were some not unexpected C_6 and C_7 fluorocarbon fragmentation products (A-D). Also isolated was an interesting range of six polyfluorocyclohexa[b]-pyridines (G-L), though only in small quantities, totalling ca. 16% by weight of the product.

The structures of these followed from elemental analysis, ir, and ^1H and ^{19}F nmr (Table 2), a self-consistent pattern being established, related to other fluoropyridines [8; 1].

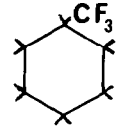
The two major products were a perfluorooctahydroquinoline, $C_9F_{15}N$ (E) and a compound F, analysing as $C_9F_{17}N$ suggesting at first the perfluoroperhydroquinoline structure (P) [9]. For these two compounds, boiling points and glc characteristics were closely related. Though it was present in fair quantity, isolation of pure E was quite difficult, and only small samples were obtained. Its structure followed from analysis, ir (C = N), and ^{19}F nmr; the peaks at 94.1 and 98.5 (AB, 2 fluorines, CF_2 - N), and



A



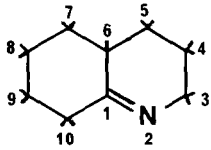
B



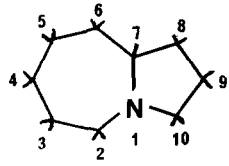
C

$n\text{-}C_7F_{16}$

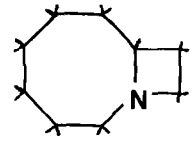
D



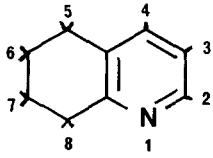
E



F



F1



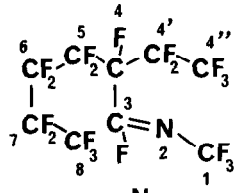
G, all F : J, 2=4=H

H, 4=H : K, 3=4=H

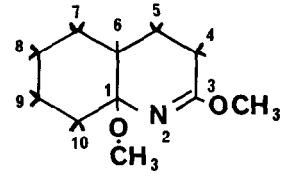
I, 2=H : L, 2=3=4=H

$CF_3 \cdot CHF \cdot (CF_2)_4 \cdot CF_3$

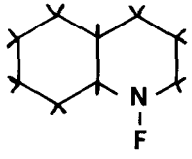
M



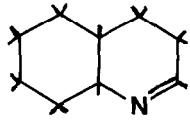
N



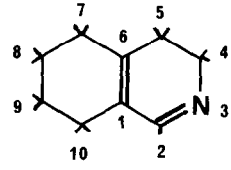
O



P



Q



R

All unmarked bonds are to FLUORINE

SCHEME

the presence of only one tertiary fluorine at 167.6 proving the compound had structure E, and was not the isomeric 2-ene (Q).

Compound E was quite reactive; even water and methanol at room temperature attacked it. The reaction with methanol afforded a dimethoxy-adduct, allocated structure O from its analysis, ir (C=N), and ^{1}H and ^{19}F nmr spectra.

Compound F was quickly found in fact not to have a quinoline-type skeleton. Only one peak for an isolated fluorine was found in the ^{19}F nmr spectrum, a tertiary $>\overset{N}{C}-F$ at 129.7 (cf. the tertiary fluorine in perfluoro-(N-cyclobutyl piperidine) [10] and that in perfluoro-(N-cyclobutyl-N'-fluoropiperazine) at ca. 137 [11]). There was nothing for N-F (usually 100-113 in perfluoropiperidines [12]), and nothing at higher field (cf. position 6 in compound E at 167.6; position 4 in N at 179.1; position 6 in O at 191.1; the tertiary fluorine in tridecafluoro-1,3-dimethyl-pyrrolidine at 184.0 [1], and that in the 1,2-isomer at 138.2 [1]). Two peaks, each an AB of 2 fluorines at low field, indicated $>CF_2$ adjacent to nitrogen. Two other AB peaks could be identified as adjacent to the tertiary fluorine. Two structures were possible therefore, and in the absence of reference compounds a distinction cannot be made by nmr spectroscopy. Both are bicyclic, with tertiary nitrogen present at a ring junction; the 7-5 fused system (bicyclo[5,3,0]; compound F), and the 8-4 fused system (bicyclo[6,2,0]; compound F1). The 7-5 system (F) is the structure preferred intuitively. Several rearrangements of pyridines to pyrrolidines are now known; during fluorinations by HVMF's [1;5;7;8], and by fluorine [13]. Further, pyrolysis of undecafluoropiperidine gives some perfluoro(1-methylpyrrolidine) [14]. Similar rearrangements to 4-membered heterocyclic rings are unreported. In our hands, very few 4-membered rings have survived [15] in the products of HVMF fluorinations, and 8 membered rings have suffered significant ruptures, whereas 5, 6, and 7 membered rings are all more stable than either. It must be admitted however that these generalisations are based on fluorinations of carbocyclic rings; among analogous nitrogen heterocycles only the N-methylpyrrolidine skeleton has been fluorinated, and it survives [16]. The preferred reaction scheme (see later) also leads to structure F.

The mass spectrum could fit either structure. Though there is a large peak (35% of base peak) at 100, suggestive of the loss of C_2F_4 from a 4-membered ring, the base peak is at 131 (C_3F_5). Several fragments seem to arise a little more plausibly from F, so perhaps on balance this structure is slightly favoured.

In contrast to E, compound F was highly stable, being recovered after long refluxing with ethanol, hydrochloric acid, or aqueous potassium hydroxide. Passage over $CsCo(III)F_4$ at 390° also left it unchanged. This strongly supports structure F or F1 with tertiary nitrogen, since perfluoro-compounds having $\rangle$N-F bonds are known to react with potassium iodide [17], as are those with piperidino-skeletons which also react with ethanol [14,18]. After 10 hours in contact with compound F, aqueous potassium iodide was free of iodine colour.

A brief re-examination of the fluorination of quinoline by cobalt(III) fluoride in a stirred reactor was next undertaken. Quite good recoveries of fluorination product were obtained at 350°. The compound present in second largest amount was perfluoroheptane (D), and the new 2H-pentadecafluoro-n-heptane (M) was found in small amount. Significant quantities of a new imine with a completely ring-opened structure were also found; tetradecafluoro-4-pentafluoroethyl-2-azaoct-2(Z)-ene (N), analogous to the ring-opened products obtained from pyridines [7;8]. The structure was shown unequivocally by ^{19}F nmr. The arrangement of the branched fluorocarbon residue was clear, all the major couplings being accounted for, and checked by decoupling experiments. The CF_3 and CF_2 groups in the C_2F_5 residue each showed apparent quartet splitting; in each case the CF_2 at position 5 and the isolated F at 3 had comparable coupling constants. The stereochemistry of CF_3 and F about the C=N double bond was Z as shown by a $CF_3N{=}C\underline{F}$ coupling constant of 15.0 [cf. 7]. The mass spectrum of compound N gave further support to the general structure proposed. Only small amounts of E were present, and the major product was compound F, identical with the sample made using caesium tetrafluorocobaltate.

The early report [9] of quinoline fluorination was by CoF_3 in a static reactor. In retrospect, it seems probable that the product obtained was complex and that the components isolated by distillation alone and in the absence of g.l.c. analysis were mixtures. Present established reactivities of compounds containing N-F bonds suggest that structure P, heptadecafluorodecahydroquinoline, was unlikely to have been present in significant quantities. Stirred reactors are now preferred because they are more compact, and they usually give higher degrees of fluorination and better yields of fluorocarbon. Further, from the molar quantities of reagents given for the static reactor experiment, good yields of highly

fluorinated products could not have been expected anyway. Isolable quantities of (P) were not present in the product of our fluorination even though work-up procedures were carefully chosen to avoid loss of reactive compounds. Nevertheless, in the 1940 s, the proposed structure (P) was quite plausible and would have been expected to be a product of this fluorination.

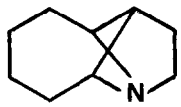
A further discrepancy arises however from a later patent claim [19], that 'perfluoroquinoline' (P) could be defluorinated by cyclopentadienyl iron in dichlorodifluoromethane, to give a mixture of bicyclic imines E + Q, which could not be separated. Characterisation was by ir and nmr, but no data were given. In the present work, pure compound E, and compound F, were individually treated with cyclopentadienyliron under conditions given in the patent [19]. F was unchanged and E very largely so, though there was a possibility that a very small amount of isomerisation might have occurred. The most likely explanation is that the starting material used in the original work [19] may have contained a little F but was largely E. The latter was presumably not removed in the purification, despite its reactivity, because there was no aqueous washing.

Isoquinoline was fluorinated over caesium tetrafluorocobaltate using conditions similar to those for quinoline, but the weight recovery was poorer. Again a complex mixture was obtained and the only products isolated were C and a new tridecafluoro-3-azabicyclo[4,4,0]decadiene with analytical and spectroscopic properties corresponding to structure R.

The fluorination of indole over caesium tetrafluorocobaltate was even less satisfactory; the product was obtained in even poorer recoveries, with no component corresponding to the original skeleton being identified.

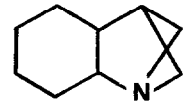
The products obtained from quinoline correspond to a fluorination pathway in which the exclusively benzenoid positions (5-8) are attacked preferentially, to the stage of saturation (compound L). The pyridine nucleus is then fluorinated 'aromatically' giving K,J,I,H and G. The rearrangement to give F as the principal product and end-stage is interesting, the bicyclic structure with no $\gtrsim$N-F bond being clearly much more stable than structure P. A possible route to F1 would be formation of a 1,4 bond to give a Dewar pyridine (this occurs photochemically with perfluoroalkylpyridines [20], though the corresponding isomers are not the predominant products) followed by rupture of the bond at the original ring fusion. However, no 4-membered rings of this type have been found among the products of any fluorinations of pyridines [1;5;7;8].

The pathway postulated earlier [1], will explain products F and N more satisfactorily, intermediates such as S and T being involved. With S, breaking of either the new (1-5; numbering as in E) or the old (6-5) bond



S

T



would give product F. With T, no corresponding product, with the perfluoro N-methyl indole skeleton (by breaking of bonds 3-5 or 4-5) was found. However, if the suggested route [1] from pyridines to open-chain aza-alkenes is followed, then production of compound N is understandable, the original "criss-cross" bonds (2-4; 3-5) failing to form, and breaking of the 1-10 bond in the carbocyclic ring, with formation of a system saturated except for a CF_3-C=N group following on.

Though structural allocations based on expected mechanistic pathways are notoriously unreliable, the applicability of the earlier postulates [1] to this case, when added to the arguments presented earlier, prompt us to assign to compound F the structure :- heptadecafluoro-1-azabicyclo[5,3,0]decane.

EXPERIMENTAL

General

Fluorination Reactors Three were used of standard design [21]. R1 was 450 mm x 45 mm int. diam., containing ca. 150 g of fluorinating agent; R2 was 1080 mm x 150 mm int. diam., containing ca. 7Kg; R3 was 1300 mm x 180 mm int. diam., containing ca. 10 Kg.

Gas-liquid chromatography Columns used were as follows:- Column a; dinonyl phthalate on 30-60 mesh Chromosorb P (1:5) in a copper tube 4.88 m x 75 mm int. diam. with a Katharometer detector: packings in glass tubes 9.14 m x 8 mm int. diam. , were used in a Pye series 104 or 105 instrument; column b, Kel F oil elastomer on 30-60 mesh Chromosorb P (1:9): column c, dinonyl phthalate on celite (1:2): column d, Ucon oil (LB 550-x) on 30-60 mesh Chromosorb P (1:4): column e, Ucon oil (50-HB-2000) on 30-60 mesh Chromosorb P (1:4): column f, polyethylene glycol adipate on 30-60 mesh Chromosorb P (1:5). Given for each separation are the column used, temperature, and nitrogen carrier gas flow rate (l/h).

Spectroscopy Infrared (ir) spectra were recorded on a Perkin-Elmer PE 257 grating instrument. Ultraviolet (uv) spectra were recorded on a Unicam SP 800A spectrophotometer. Mass spectra were obtained using AEI MS9 and MS 20 instruments. Nuclear magnetic resonance (nmr) spectra were measured on Perkin Elmer R10 or R12B spectrometers at 60 MHz for ^{1}H and 56.4 MHz for ^{19}F. Chemical shifts are given in τ units, p.p.m. downfield of internal tetramethylsilane (^{1}H) and in δ units, p.p.m. upfield of internal trichlorofluoromethane (^{19}F). Spectra were run in carbon tetrachloride solutions unless otherwise stated. ^{19}F and ^{1}H nmr data for the fluorocyclohexa[b]pyridines are recorded in Table 2. ^{19}F and ^{1}H nmr data for other compounds are given in the text, listed in the order:- chemical shift position and type of signal, coupling constant, relative intensity (in brackets), ring position from formulae in the Scheme.

Fluorination of quinoline with caesium tetrafluorocobaltate Quinoline (700 g total, in batches of 50 g) was passed into the reactor (R2) at 335-350° (input rate 25 g h^{-1}). The combined products (1520 g) were washed with water, then with saturated sodium bicarbonate solution, dried ($MgSO_4$) and filtered. A portion (831 g) was distilled through a vacuum-jacketed column (1.22 m x 25 mm) packed with Dixon gauzes to give 17 fractions:- 1, b.r.<120°; 2-17, b.r. 120-148°; and 18, still residue b.r. > 148° (173 g).

Fraction 18 was distilled through a smaller column (0.61 m x 20 mm) to give 9 further sub-fractions 18(i) - 18(ix). Fraction 18(ix) was the still residue which was separated by free flaming at 0.1 mm pressure into 18(1x)a, a pale orange liquid, and a black solid residue, 18(ix)b.

Glc analyses and glc separations in some cases of these fractions allowed the approximate product distribution given in Table 1 to be calculated.

New compounds were isolated by glc as follows:- The bulk (32.7)g of fraction 3, b.r. 123.0-124.5 (34.1 g) (a, 44°, 75) gave 4 sub-fractions; 3(iii) was further separated (b, 56°, 7.5) and the middle cut 3(iii)b re-separated (c, 60°, 7.5) to give pentadecafluoro-2-azabicyclo[4,4,0]dec-1-(2)-ene (E), nc, b.p. 125° (Found: C, 26.35, F, 70.3. $C_9F_{15}N$ requires C, 26.55; F, 70.0%), m/e 406.975 (M; requires 406.979); ir 1708 (w) (C=N) and 1206 (vs) cm^{-1}: ^{19}F nmr; 94.1 and 98.5 AB, J_{AB}=258, (2), 3; 104.2-146.0, (12), 4,5,7,8,9 and 10; 167.6 c, (1), 6. A portion (78.8 g) of fractions 13 and 14, b.p. 129° (80.5 g), largely F, was separated (a, 59°, 75) into 3 sub-fractions, the centre one (33.3 g) after further glc (c, 70° 6.0) giving heptadecafluoro-1-azabicyclo[5,3,0]decane

TABLE 1

Estimated weights of compounds present in fractions

Compound (see Scheme)	No.	Fractions 1	2-14	15	16	17	18	Total
	Wt (g)	124.2	401.2	27.6	25.6	9.7	173.0	761.3
A		31.2	-	-	-	-	-	31.2
B		11.7	-	-	-	-	-	11.7
C		8.1	-	-	-	-	-	8.1
D		10.4	-	-	-	-	-	10.4
E		25.2	171.6	0.4	-	-	-	197.2
F		8.4	189.8	14.1	7.1	1.2	-	220.6
G		-	-	3.0	11.9	5.5	8.3	28.7
H		-	-	-	0.5	0.4	8.2	9.1
I		-	-	-	-	-	8.5	8.5
J		-	-	-	-	-	13.3	13.3
K		-	-	-	-	-	14.3	14.3
L		-	-	-	-	-	45.6	45.6
								598.7

(F), nc, b.p. 128-129° (Found: C, 24.5; F, 73.0. $C_9F_{17}N$ requires C, 24.3; F, 72.6%): ir 1234 cm^{-1}: ^{19}F nmr; 86.9 and 90.3 AB, J_{AB}=178, (2), 10; 90.1 and 95.5 AB, J_{AB}=220, (2), 2; 119.7 c, (2), 6; 125.2 and 137.0 AB, J_{AB}=248, (2), 8: 128.7 c, (8), 3,4,5 and 9; 129.7 (c), (1), 7: mass spectrometry gave the following significant peaks (mass number, formula, fragment lost, % intensity of base peak); 445, $C_9F_{17}N$, molecular ion, 3.4; 426, $C_9F_{16}N$, -F, 19.4; 376, $C_8F_{14}N$, $-CF_3$, 3.1; 326, $C_7F_{12}N$, $-C_2F_5$, 3.5; 295, $C_6F_{11}N$, $-C_3F_6$, 3.3; 181, C_4F_7, $-C_5F_{10}N$, 6.1; 176 C_4F_6N, $-C_5F_{11}$, 6.5; 169, C_3F_7 $-C_6F_{10}N$, 8.0; 150, C_3F_6, $-C_6F_{11}N$, 14.7; 145, C_3F_5N, $-C_6F_{12}$, 6.6; 131, C_3F_5, $-C_6F_{12}N$, 100; 119, C_2F_5 $-C_7F_{12}N$, 9.2; 114, C_2F_4N, $-C_7F_{13}$, 7.7; 100, C_2F_4 $-C_7F_{13}N$, 34.5; 93, C_3F_3, $-C_6F_{14}N$, 4.1; 69, CF_3, $-C_8F_{14}N$, 52.2.

Part of fraction 18(iv) (3.33 g) gave by glc (d, 148°, 4.5) 9 sub-fractions. The 2nd was undecafluorocyclohexa[b]pyridine (G), b.p. 163° (Found: C, 32.8; F, 62.8; N, 4.1. Calc. for $C_9F_{11}N$: C, 32.6; F, 63.1; N, 4.2%): m/e 331 (M), 312 (M-F): ir 1631 (s), 1604 (s), 1509 (vs) and 1470 (s) cm^{-1}. The spectroscopic properties corresponded with those reported [22] previously for a sample isolated from the heptachloroquinoline/KF reaction.

The 4th sub-fraction of 18(iv) was 2,3,5,5,6,6,7,7,8,8-decafluorocyclohexa[b]pyridine (H), nc, b.p. 169.5-170-5° (Found: C, 34.5; H, 0.6; F, 60.8; N, 4.7. $C_9HF_{10}N$ requires C, 34.5; H, 0.3; F, 60.7; N, 4.5%: ir 3074 (w) ≷ C-H, 1621 (m), 1608 (m), 1496 (s), 1485 (s) cm^{-1}.

The 6th sub-fraction of 18(iv) was 3,4,5,5,6,6,7,7,8,8-decafluorocyclohexa[b]pyridine (I), nc, b.p. 171.5-172.5° (Found: C, 34.7; H, 0.2; F, 60.9; N, 4.5%): ir 1624 (s), 1587 (m), 1500 (s) cm^{-1}.

The 8th sub-fraction of 18(iv) was 3,5,5,6,6,7,7,8,8-nonafluorocyclohexa[b]pyridine (J), nc, b.p. 174-176° (Found: C, 36.5; H, 0.9; F, 57.9; N, 5.0. $C_9H_2F_9N$ requires C, 36.6; H, 0.7; F, 57.9; N, 4.75%): ir 3081 (w) ≷C-H, 1612 (s), 1589 (m), 1468 (s) cm^{-1}.

Fraction 18(ix)a was separated by glc (e, 166°, 6.0) into 5 sub-fractions. The 2nd was 2,5,5,6,6,7,7,8,8-nonafluorocyclohexa[b]pyridine (K), nc, b.p. 190.5-192.5°, m.p. 22.5-24.5° (Found: C, 36.8; H, 0.6; F, 57.9; N, 4.5%): ir 3105 (w) ≷C-H, 1607 (s), 1482 (s) cm^{-1}.

The 4th sub-fraction of 18(ix)a was 5,5,6,6,7,7,8,8-octafluorocyclohexa[b]pyridine (L), nc, b.p. 199-200°, m.p. 34-36° (Found: C, 39.0; H, 1.3; F, 54.7; N, 5.5. $C_9H_3F_8N$ requires C, 39.0; H, 1.1; F, 54.8; N, 5.1%): ir, 3070 (m), 3030 (m) ≷CH, 1598 (s), 1587 (m) 1464 (m) and 1452 (m) cm^{-1}.

Fluorination of quinoline with cobalt(III) fluoride Quinoline (1300 g total, in portions of 100 g or 150 g) was passed into the reactor (R3) which was at 350° (input rate 50 g h^{-1}). The combined products were washed with water, separated (3300 g), washed with sodium bicarbonate solution and dried ($MgSO_4$). The bulk of the material (2775 g) was distilled through a vacuum-jacketed column (1.22 m x 25 mm) packed with Dixon gauzes. Gaseous material [$(CF_3)_2NH$?] was evolved and since traces of hydrogen fluoride were then present, solid calcium carbonate was added to the still pot. Fractions obtained were: numbers 1-4, b.r. 23-80° (303 g) unidentified compounds + product D; 5, b.p. 80-81° (338 g) hexadecafluoro-n-heptane (D) (correct ir); 6, b.r. 81-87°, (38 g) unidentified + D + M; 7, b.r. 87-93° (31 g), impure M; 8, b.r. 93-100° (39 g) unidentified + M + N; 9-12, b.r. 100-123° (405 g) N + F + unknowns; 13-15, b.r. 123-126° (381 g) largely F; 16, b.p. 126-127° (690 g), F; 17, b.r. >127° (480 g) largely F. Gas chromatographic analysis indicated the major products to be F, D, and N in approximate relative proportions 4:1.5:1.

Fraction 7 (1.38 g) was purified by glc (b, 50°, 5.5) to give 2H-pentadecafluoro-n-heptane (M), nc, (0.67 g), b.p. 85.5-87° (Found: C, 23.0;

H, 0.25; F, 76.7. C_7HF_{15} requires C, 22.7; H, 0.3; F, 77.0%): ir 1245, 1213 cm^{-1}: nmr; ^1H, 4.98 cd, J 43.5; ^{19}F, 74.6, (3), 1; 81.7, (3), 7; 123.5, (6), 3,4,5; 126.8, (2), 6; 213.3 cd J ca. 45 (1), 2; all complex.

Fraction 11 (b.r. 116-120°; 59 g) was separated by glc (c, 64°, 6.0; 1.98 g) to give: (i) tetradecafluoro-4-pentafluoroethyl-2-azaoct-2(Z)-ene (N), nc, (0.73 g) b.p. 117.5-119.5° (Found: C, 22.6; F, 74.55; N, 2.9. $C_9F_{19}N$ requires C, 22.4; F, 74.7; N, 2.9%): ir 1771 (C=N), 1240 cm^{-1}: ^{19}F nmr (pure liquid); Varian XL 100 machine at 94.1 MHz, 13.6 b, (1) 3; 57.6 d, J_{13}=15.0, (3) 1; 80.4 dq, $J_{4"4}$=13.0, $J_{4"5} \sim J_{4"3} \sim 3$, (3) 4"; 81.2 tt, J_{86}=10.4, J_{85}=2.8, (3) 8; 114.3 b, (2) 5; 116.0 Aq and 121.6 Bc AB, J_{AB}=287, $J_{4'A5} \sim {}^{4'A3} \sim 15.7$, (4'A=1) 4'; 119.7 b, (6 + 4'AB=4) 6; 125.6 ct, $J_{75} \sim 16$, (2) 7; 179.1 b, (1) 4: mass spectrometry (as for compound F); 464, $C_9F_{18}N$, -F, 2.9; 376, $C_8F_{14}N$, $-CF_5$, 2.9; 219, C_4F_9, $-C_5F_{10}N$, 4.7; 181, C_4F_7, $-C_5F_{12}N$, 2.4; 176, C_4F_6N, $-C_5F_{13}$, 5.2; 169, C_3F_7, $-C_6F_{12}N$, 4.2; 131, C_3F_5, $-C_6F_{14}N$, 15.0; 119, C_2F_5, 22.8; 114, C_2F_4N, 26.5; 100, C_2F_4, 7.7; 69, CF_3, 100 with small peaks at 326, 314, 276, 245, 231, and 226: (ii) a mixture (0.4 g) containing (i) and several other compounds: (iii) a mixture (0.25 g). This was further separated by glc (b, 64° 6.0) into roughly equal amounts of pentadecafluoro-2-aza-bicyclo[4,4,0]dec-1(2)-ene (E), and heptadecafluoro-1-azabicyclo[5,3,0]-decane (F) both identified by ir.

Fractions 13-17 were very largely F and 16 was a fairly pure sample (ir).

Non-reactivity of heptadecafluoro-1-azabicyclo[5,3,0]decane (F)

Separate reactions were carried out using ferrocene [F (0.6 g), ferrocene (0.75 g), CCl_2F_2 (10 cm^3), 2 weeks at 15°, details as below], ethanol [F (5.0 g), EtOH (20 cm^3), 3 days under reflux], hydrochloric acid [F, (5.0 g), HCl (18%, 20 cm^3) 3 days under reflux], aqueous potassium hydroxide [F (5.0 g), KOH (20%, 20 cm^3), 3 days under reflux], caesium tetra-fluorocobaltate [F (2 x 4.0 g), reactor R1, 390°]. In all cases there were no signs of reactions and good recoveries of F were obtained.

With aqueous potassium iodide [F (0.1 g), KI (30%, 2 cm^3), 10 h at 15°] no colour developed and F was unchanged. Undecafluoropiperidine reacted under the same conditions to give an intense colour due to liberation of iodine.

TABLE 2

^{1}H and ^{19}F nmr spectrà of fluorocyclohexa[b]pyridines

Compound	Ref. No.	^{1}H 2	^{1}H 3	^{1}H 4	^{19}F 2	^{19}F 3	^{19}F 4	^{19}F 55'	^{19}F 66'	^{19}F 77'	^{19}F 88'
Perfluoro	G	-	-	-	(72.4) 71.0dd J_{24}30.0 J_{23}24.0	(154.7) 154.1ddt J_{32}23.6 J_{34}17.6 J_{38} 2.8	(115.6) 116.9ddt J_{42}29.6 J_{43}17.2 J_{45}16.8	107.7c or 112.1c	135.0c or 136.0c	135.0c or 136.0c	107.7c or 112.1c
4H-	H	-	-	2.01dd J_{42}7.8 J_{43}7.8	(77.3) 75.2cd J_{23}23.7	(133.6) 129.2cd J_{32}23.7	-	104.5c or 110.4c	134.9c		104.5c or 110.4c
2H-	I	1.05cd J_{24} 7.8	-	-	-	(142.0) 142.7cd J_{34}19.2	(122.6) 123.8dtd J_{43}19.0 J_{45}16.0 J_{42} 7.8	106.8c or 110.7c	134.7c or 135.5c	134.7c or 135.5c	106.8c or 110.7c
2H,4H-	J	1.08cd J_{24} 2.3	-	2.08dd J_{43}7.1 J_{42}2.3	-	(120.9) 117.4c	-	104.9c or 109.7c	134.9c		104.9c or 109.7c

3H,4H-	K	-	2.66dd J_{34} 8.7 J_{32} 3.3	1.72dd J_{43} 8.7 J_{42} 6.0	(58.5) 56.7c	-	-	104.5c or 111.6c	135.0c	104.5c or 111.6c
2H,3H,4H-	L	0.95d J_{23} 4.5	2.25dd J_{34} 8.4 J_{32} 4.5	1.75d J_{43} 8.4	-	-	-	104.8c or 110.5c	134.8c	104.8c or 110.5c

Relative intensities of all peaks are as expected.

Figures in brackets above the aromatic ^{19}F values are the chemical shifts calculated from the data of Table 4 Reference [1], assuming the changes induced by the perfluoro-ring are the same as those for two CF_3 groups, in the 5 and 6 positions.

Reactions of pentadecafluoro-2-azabicyclo[4,4,0]dec-1-(2)-ene (E)

(a) With water Compound E in admixture with F (60:40; 2.0 g) was shaken at 15° with water (2 cm^3). After 18 h, 3 layers were present and after 64 h further the system had reverted to 2 layers. The lower layer was shown by ir to be compound F, no unsaturation being detectable. The aqueous layer was extracted with ether but the product decomposed on attempted isolation.

(b) With methanol Compounds E + F (60:40; 2.0 g) and dry methanol (2.0 g) were mixed and kept at 15°, the reaction being monitored by analytical glc. After 3 h, glc separation (f, 141°, 5.0) gave (i) (by ir) impure F (0.74 g); (ii) F + methanol + 0 (0.06 g); (iii) impure methanol; (iv) tridecafluoro-1,3-dimethoxy-2-azabicyclo[4,4,0]dec-2-ene (0), nc, (0.74 g) b.p. 213-215° (Found: C, 30.7; H, 1.6; F, 57.7, N, 3.0. $C_{11}H_6F_{13}NO_2$ requires C, 30.6; H, 1.4; F, 57.3, N, 3.25%): ir 2967 (w, CH) 1677 (C=N) cm^{-1}: nmr; ^1H, 6.48 s, (1), 1; 5.99 s, (1), 3; ^{19}F, 108.7-139.1, (12), 4,5,7,8,9,10; 191.1 c, (1), 6: (v) (by ir) impure E (0.05 g).

(c) With ferrocene Compound E (0.6 g) was introduced into a Carius tube (20 cm^3), containing ferrocene (0.75 g) dissolved in dichlorodifluoromethane (10 cm^3), and cooled by liquid N_2 [cf. 19]. The tube was sealed and periodically shaken at 15° during 2 weeks, after which the only volatile components positively detected were CCl_2F_2 and compound E (ir) with a very small proportion of impurity present.

Fluorination of isoquinoline with caesium tetrafluorocobaltate

Isoquinoline (6.0 g, in 2 batches) was passed into reactor (R1) at 335-340° (input rate 9 gh^{-1}). The combined products (7.8 g) were washed (cf. quinoline fluorination), dried $MgSO_4$, and a portion (3.08 g) separated by glc (c, 95°, 6.0) to give (i) 1:1 mixture (0.23 g) of C and an unidentified compound; (ii) C (0.48 g); (iii) a mixture (0.47 g) of C and 2 unidentified products; (iv) a mixture (0.46 g) of 4 unidentified products, (v) a mixture (0.49 g) mainly another unidentified product together with those of fraction (iv) and R; (vi) tridecafluoro-3-azabicyclo[4,4,0]deca-1(6)-2-diene (R), nc, (0.25 g), b.p. 122.5-124.5° (Found: C, 29.2; F, 66.8. $C_9F_{13}N$ requires C, 29.3; F, 66.9%): m/e 369 (M), 350 (M-F), 331 (M-2F): ir 1721 (s) 1680(w)cm^{-1}: uv, λ max (cyclohexane) 226 nm (ε 2,250): ^{19}F nmr (pure liquid); 36.8 c,(1) 2; 104.1 c,(2) 4; 113.0 c,(2) 5 or 7; 114.5 c,(2) 5 or 7; 123.8 c,(2) 10; 134.7 c,(2) 8 or 9; 135.8 c,(2) 8 or

9. Compound R had decomposed after being kept for several weeks. Larger scale fluorination (Reactor R2 at 300°) gave a similar product range.

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REFERENCES

1 Part 7 of this series; R.G. Plevey, R.W. Rendell, and J.C. Tatlow, J. Fluorine Chem., 21 (1982) 265.
2 A.J. Edwards, R.G. Plevey, I.J. Sallomi, and J.C. Tatlow, J. Chem. Soc., Chem. Comm., (1972) 1028.
3 R.G. Plevey, I.J. Sallomi, D.F. Thomas, and J.C. Tatlow. J. Chem. Soc. Perkin I, (1976) 2270.
4 J.C. Tatlow, R.G. Plevey, and A.J. Edwards, to I.S.C. Chemicals Ltd., B.P. 1,392,571 (1975).
5 R.G. Plevey, R.W. Rendell, and J.C. Tatlow, J. Fluorine Chem., 21 (1982) 159.
6 R.N. Haszeldine, J. Chem. Soc., (1950) 1966: Idem, Ibid, (1950) 1638.
7 P.L. Coe, J.C. Tatlow, and M. Wyatt, J. Chem. Soc. Perkin I, (1974) 1732.
8 P.L. Coe, A.G. Holton, and J.C. Tatlow, J. Fluorine Chem., 21 (1982) 171.
9 R.N. Haszeldine and F. Smith, J. Chem. Soc., (1956) 783.
10 R.E. Banks, K. Mullen, and G.E. Williamson, J. Chem. Soc. (C), (1968) 2608.
11 R.E. Banks, P.A. Carson, and R.N. Haszeldine, J. Chem. Soc. Perkin I, (1973) 1111.
12 C.H. Dungan and J.R. Van Wazer, Compilation of Reported ^{19}F Nmr Chemical Shifts, Wiley-Interscience, New York, 1970.
13 R.E. Banks and G.E. Williamson, J. Chem. Soc., (1965) 815.
14 R.E. Banks, W.M. Cheng, and R.N. Haszeldine, J. Chem. Soc., (1962) 3407.
15 Very recently a cyclobutane ring has survived in the addition of fluorine to a highly substituted perfluorocyclobutene using cobaltic fluoride at 310°: see P.L. Coe, S.F. Sellers, J.C. Tatlow, H.C. Fielding, and G. Whittaker, J. Fluorine Chem., 18 (1981) 417.
16 P.L. Coe, P. Smith, J.C. Tatlow and M. Wyatt, J. Chem. Soc. Perkin I, (1975) 781.

17 J.A. Cuculo and L.A. Bigelow, J. Amer. Chem. Soc., 74 (1952) 710; J.A. Young, W.S. Durrell, and R.D. Dresdner, ibid., 81 (1959) 1587.

18 R.E. Banks and E.D. Burling, J. Chem. Scc., (1965) 6077.

19 R.A. Mitsch (to M.M.M. Co.), U.S.P. 3,674,785 (1972).

20 R.D. Chambers and R. Middleton, J. Chem. Soc. Chem. Comm., (1977) 154.

21 M. Stacey and J.C. Tatlow, Advances in Fluorine Chemistry, Butterworth: London, 1 (1960) 166.

22 P. Sartori, K. Ahlers, and H.J. Frohn, J. Fluorine Chem., 7 (1976) 363.