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POLYFLUOROBICYCLO 4, 4, 0 DECANES. PART II. THE FLUORINATION OF TETRALIN BY POTASSIUM TETRAFLUOROCOBALTATE(III)

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SUMMARY

Fluorination of tetralin, using potassium tetrafluorocobaltate(III) at 275-300 °C, gave a series of compounds with bicyclo[4,4,0]decane skeletons, as follows:- hexadecafluoro-1(6)-ene (1); tetradecafluoro-1(6),3(4)-diene (2); 3H-pentadecafluoro-1(6)-ene (3); perfluorotetralin (6) (all reported earlier); 8H-tridecafluoro-1(6),3(4)-diene (4); 3H,4H-tetradecafluoro-1(6)-ene (5); a mixture of 3H,8H- and 3H,9H- tetradecafluoro-1(6)-ene (7 and 8); 2H-undecafluorotetralin (9); 3H,4H,8H-tridecafluoro-1(6)-ene (10). The structures of all the new products (4,5,7-10) were determined by elemental analysis, proton and fluorine nmr, and mass spectrometry. Obviously, with this reagent, the residual 1(6) double bond and the β-hydrogens are the most difficult to replace.

INTRODUCTION

Tetralin was fluorinated exhaustively with cobalt trifluoride long ago, giving perfluorodecalin [1], and the process has been optimised for its production for use as a component of a blood substitute [2]. At lower temper-

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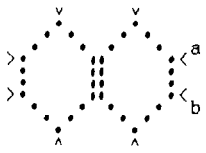
atures, the reaction afforded [3] not only *cis*- and *trans*- perfluorodecalin, but also a series of stereoisomeric heptadecafluorodecalins, together with hexadeca- and 3H-pentadeca- fluorobicyclo-[4,4,0]dec-1(6)-ene (1 and 3: see Scheme). A preliminary study using the milder reagent potassium tetrafluorocobaltate(III) has also been reported [4]. The mixture obtained consisted of three major components (1-3), together with unidentified higher-boiling products. Fluorination [5] using caesium tetrafluorocobaltate(III) afforded compound (1) and perfluorotetralin (6). The same products respectively arose from naphthalene [4], and from naphthalene and decalin [4,5].

The present paper describes our further studies on the fluorination by potassium tetrafluorocobaltate(III), and the identification of many of the higher-boiling components encountered earlier.



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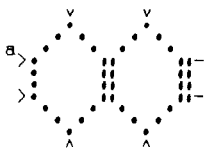
3: a = H; b = F
5: a = b = H



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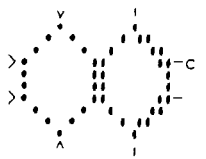

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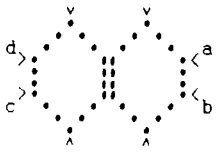
9: c = H



7) {a = c = H; b = d = F
8) {a = d = H; c = b = F
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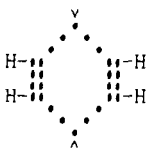
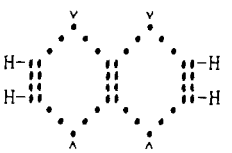


A



B

ALL UNMARKED BONDS ARE TO FLUORINE

SCHEME

RESULTS

The fluorination process was as reported before [4], and pure products were obtained after fractional distillations, followed by gas-liquid chromatographic (glc) separations as recorded in the Experimental section.

The molecular formulae of the new products isolated were determined by elemental analysis and mass spectrometry (molecular ion peaks were usually small), and corresponded to the compound numbers (see Scheme) as follows:-

4	5	6	7 + 8	9	10
$C_{10}HF_{13}$	$C_{10}H_2F_{14}$	$C_{10}F_{12}$	$C_{10}H_2F_{14}$	$C_{10}HF_{11}$	$C_{10}H_3F_{13}$

In the ^{19}F nmr spectra of all of these compounds there was an absence of peaks in the standard region for tertiary fluorine $(R_F)_3C\text{-}\underline{F}$, showing that they had a double bond in the 1(6)-positions, or an arene ring.

Product (4) had nmr peaks for a >CHF and three $>CF_2$ groups in positions very close to those allocated to the corresponding groups in the hydrogen-containing ring of the known compound (3) (see Table 1). Also present was a complex doublet and a complex singlet, which could be allocated respectively to two vinylic fluorines, and to two $>CF_2$ groups located immediately between double bonds. The mass spectra of both compounds (3 and 4) showed a major fragment with mass number corresponding to the loss of a C_2HF_3 unit from the molecular ion. These data all indicate that compound (4) has the structure 8H-tridecafluorobicyclo[4,4,0]deca-1(6),3(4)-diene.

Compound (5) was shown by nmr to have a symmetrical structure; only one type of β-HFC< group was present. The compound was 3H,4H-tetradecafluorobicyclo[4,4,0]dec-1(6)-ene, as was shown by the following observations:- (i) one of the major fragments in the mass spectrum corresponded to the loss of the unit $C_2H_2F_2$, whereas that from loss of C_2HF_3 gave rise to a very minor peak only; (ii), the ^{19}F nmr spectrum of (5) had peaks close to those allocated to the 8/9 positions of (3); (iii) the other two symmetrical isomers of this type (7 and 8) were isolated as a mixture; their spectroscopic parameters fitted much better for the structures with a β-HFC< moiety in each ring.

Compound (6) was the known perfluorotetralin [5].

The fourth new product appeared, by glc, to be pure. However, ^{19}F nmr showed that two closely-related compounds were present, in roughly similar amounts. As indicated above, both components were symmetrical, and only one type of >CHF group (in the β-position) was present. However, there were no peaks resembling closely those found in the spectrum of compound (3) for the two $>CF_2$ groups in the 8/9 positions. In the mass spectrum, the peaks from loss, by the molecular ion, of C_2HF_3 and of $C_2H_2F_2$ were, respectively, large and very small. Thus the mixture consisted of two products (7 and 8), and their structures were 3H,8H- and 3H,9H- tetradecafluorobicyclo[4,4,0]dec-1(6)-ene. No separation of them could be achieved.

The peak in the ^1H nmr spectrum of compound (9) was a doublet of triplets in the aromatic region. Also, the ^{19}F spectrum fitted best for the presence of β-H in an arene ring. The major mass spectral peak was that from the molecular ion less C_2F_4, followed by that from the molecular ion itself. Hence, this product was 2H-undecafluorotetralin (9).

Product (10) had major mass spectral peaks from fragments arising from the loss of C_2HF_3, and of $C_2H_2F_2$, from its molecular ion: loss of C_2F_4 gave rise to a scarcely observable peak in this case. The suggested structure was supported by the ^1H and ^{19}F nmr spectra; it was 3H, 4H, 8H-tridecafluorobicyclo-[4, 4, 0]dec-1(6)-ene.

The higher-boiling fractions of the mixture from the fluorination consisted of relatively small amounts of other compounds, but pure samples could not be obtained. Another 3H, 4H, 8H-tridecafluoride appeared to be present; presumably, it was a stereoisomer of compound (10). From one experiment, a sub-fraction was isolated, containing a compound which was possibly a 3H, 4H, 8H, 9H-dodecafluoride (11), but this could not be confirmed.

An interesting feature of the mass spectra of these bicyclo[4, 4, 0]dec-1(6)-enes was a breakdown pathway of the retro-Diels-Alder type, presumably arising from the presence of the 1(6) double bond. Fragments formed by the loss of the appropriate C_2-units from both the 3/4 and 8/9 positions of the bicyclic structure gave major peaks in all cases. Furthermore, for compounds with hydrogen in one ring only (3 and 5), loss of hydro-fluoro-ethene units occurred preferentially to that of C_2F_4. Peaks from units arising by loss of HF from the molecular ion were barely detectable, however. The tetralins (compounds 6 and 9) also lost a C_2 unit, tetrafluoroethene in both cases, to give their base peaks, larger than those from the molecular ions.

DISCUSSION

The pathway for this fluorination of tetralin probably involves aromatization early on, the products from naphthalene being similar [4]. A logical assumption is that it then follows a course related to that for benzene, for which the key intermediate is 3, 3, 6, 6-tetrafluorocyclohexa-1, 4-diene (A) [6] and various possible pathways have been evaluated [7]. From related reactions previously reported for naphthalene [cf 7], the tri-ene (B) is the key intermediate expected in this case, arising *via* 1:4-additions.

$KCoF_4$ gives high proportions of unsaturated fluorohydrocarbons from the fluorination of monocyclic arenes [6,8]. The 1(6) double bond is frequently present in the products when polyfluorides are generated from the naphthalene system [3,5,9], presumably because approach of reagents is hindered, and the saturated ring system is, relatively, a little more strained. This bond is unlikely to be saturated by $KCoF_4$ and its presence in all these compounds (1-10) is understandable therefore. Also, it will facilitate the saturation of the other double bonds in reaction intermediates; those present in diene systems are fluorinated more readily than are isolated ones.

The intermediacy of tri-ene (B) seems certain therefore, and addition of fluorine across the 3/4 and 8/9 double bonds must surely follow, leading to compounds of the type of structure (11), and thence to other products.

The nmr peaks for the >CHF groups of the 1(6)-ene products (3, 4, 5, 7, 8, 10) indicate that there is only one type of grouping present in each, and the respective chemical shift values for all (H, ≈ 5·1; F, ≈ 217), lie quite close together. It follows from this, not only that these groups are in β-positions, but that they are all equivalent stereochemically, ie where they are adjacent, in -CHF·CHF- units, the fluorines are arranged *trans*. These conclusions are based on related ^{19}F nmr data for polyfluorocyclohexanes [10], and on the preferential formation [11] of *trans*-CHF·CHF- systems (not always the major products), when fluoro-cyclo-enes with >HC=CH< units were fluorinated over $KCoF_4$: this gave products with *trans*-stereochemistry from toluene [8], and from benzene [6] (very largely). In contrast, if 1H,2H-octafluorocyclohexene was fluorinated over CoF_3, the major products [12] were 1H,2H-decafluorocyclohexanes, with a *trans*- to *cis*-ratio of 1·7:1 (the major product [11] from $KCoF_4$ was 1H-nonafluorocyclohexene). However, *cis*-isomers are known to eliminate HF to give enes much more readily than do the *trans* ones [13; some mechanistic detail in 14]; such loss can occur in the presence of heated ionic fluorides [cf 15], and dehydrofluorination stages have been demonstrated in fluorinations by $KCoF_4$ [11]. Therefore, the conclusion reached above, that the products are *trans*, is not invalidated.

Another, inter-related, branch of the fluorination pathway could invoke direct aromatic substitution, perhaps of more significance with the complex fluorides than with CoF_3 [7]. It seems likely to be involved in fluorinations with $CsCoF_4$ [16]. This route may simply be a branch off the main pathway, as has been pointed out before [7]. From the probable key intermediate (B), saturation of the HC=CH bonds would give (11). Also with (B) however, a 1:3 fluorine shift could occur, to be followed rapidly by HF loss to give

reversion to a trifluoro-arene ring with β-H; *ie* the orientation of tetralin (9). A second such sequence would give a perfluoro-arene ring. Similar 1:3 shifts of fluorine in monocyclic fluoro-dienes have been reported [17, 18, 19] and among aspects studied [18], has been the generation of fluoro-arenes.

By these two branches of the pathway, all the products so far isolated from the tetralin/$KCoF_4$ reaction can be realized. The $-(CF_2)_4-$ fragment can arise from complete replacement of H in -CHF·CHF-, or, perhaps more plausibly, by the ultimate saturation of a perfluoarene ring. In any event, whatever the details of the reaction path, there is clearly special significance in the presence, in all these products, both cycloalkenes and arenes, of the residual H exclusively in β-positions, and mainly in >CHF functions.

EXPERIMENTAL

Fluorination of Tetralin

The conditions were broadly as before [4], though recoveries of fluoro-product were better. Tetralin (100 g) was passed in a stream of nitrogen (20 lh^{-1}) over $KCoF_4$ at 270 °C. Crude product (ca 200 g) was processed, combined and fractionally distilled as before through the packed 1·3 m column. The material b.p. 150-170 °C (mainly) was analysed by glc (Pye 105 machine; PEGA column [4] at 150 °C). There were 6 major peaks, corresponding to product numbers and proportions (from peak areas) as follows: 4, 12%; 5, 14%; 6, 28%; 7 + 8, 10%; 9, 15%; 10, 12%; unidentified products, 9%.

To isolate pure samples, this material was redistilled through the same column and individual fractions then distilled through a Spaltrohr 500 unit, so as to maximise the concentration of each product in a sub-fraction. Pure compounds were then isolated by glc using a Pye 105 machine (columns, 9 m x 9·5 mm: a, UCON [3]; b, PEGA [4]) as follows:

Compound Number	Column	Temperature (°C)	Retention Time (min)	Nitrogen Pressure (psi)
4	a	110	28-31	20
5	a	110	48-51	20
6	a	130	25-29	20
7 + 8	a	130	50-54	20
9	b	153	30-33	30
10	b	165	75-80	30

Analytical Data for the Compounds Isolated

Mass spectra were measured on a Kratos machine. After the molecular ion peak (small unless stated otherwise), are listed those which gave structural information, in decreasing order of intensity. For all except compound (6), major peaks were present at 69(CF_3); 51(CHF_2); 113(C_3HF_4) (not for product 5); 131(C_3F_5); 93(C_3F_3); those at 51 and 113 being small for product (9).

(3): 3H-Pentadecafluorobicyclo[4,4,0]dec-1(6)-ene [4,3]: M/e, 406(M): 324 ($M-C_2HF_3$); 255($M-C_3HF_6$); 205($M-C_4HF_8$); 82(C_2HF_3); 155($M-C_5HF_{10}$); 287($M-C_2F_5$); 306($M-C_2F_4$); 387(M-F).

(4): 8H-Tridecafluorobicyclo[4,4,0]dec-1(6),3(4)-diene (nc); b.p. 135 °C; (Found: C, 32·5; H, 0·4. $C_{10}HF_{13}$ requires C, 32·6; H, 0·3%): M/e, 368 (M): 217($M-C_3HF_6$); 236($M-C_3HF_5$); 286($M-C_2HF_3$); 267($M-C_2HF_4$); 249 ($M-C_2F_5$); 299($M-CF_3$); 82(C_2HF_3); 186((($M-C_4HF_7$); C_6F_6); 349(M-F); 368.

(5): 3H,4H-Tetradecafluorobicyclo[4,4,0]dec-1(6)-ene (nc); m.p. 34-36 °C; (Found: C, 31·2; H, 0·6; F, 68·9. $C_{10}H_2F_{14}$ requires C, 30·9; H, 0·5; F, 68·6%): M/e, 388(M): 324($M-C_2H_2F_2$); 255 ($M-C_3H_2F_5$); 95($C_3H_2F_3$); 205($M-C_4H_2F_7$); 64($C_2H_2F_2$); 269 ($M-C_2F_5$); 369(M-F); 288($M-C_2F_4$).

(6): Dodecafluorotetralin [20,5]; m.p. 20 °C: M/e, 348(M): 248($M-C_2F_4$); 348(M); 329(M-F); 279($M-CF_3$); 298($M-CF_2$); 179($M-C_3F_7$); 229 ($M-C_2F_5$); 198($M-C_3F_6$); 241($M-CF_5$); 210($M-C_2F_6$); 260($M-CF_4$).

(7+8): Mixture of 3H,8H- and 3H,9H-Tetradecafluorobicyclo[4,4,0]dec-1(6)-ene (nc); b.p. 141 °C; (Found: C, 30·7; H, 0·5. $C_{10}H_2F_{14}$ requires C, 30·9; H, 0·5%): M/e, 388(M): 306($M-C_2HF_3$); 237($M-C_3HF_6$); 113(C_3HF_4); 82 (C_2HF_3); 218($M-C_3HF_7$); 187($M-C_4HF_8$); 168($M-C_4HF_9$); 137($M-C_5HF_{10}$); 199($M-C_3HF_8$); 299($M-CHF_4$); 287($M-C_2HF_4$); 369(M-F); 319($M-CF_3$).

(9): 2H-Undecafluorotetralin (nc); b.p. 150 °C; (Found: C, 35·8; H, 0·4; F, 63·3. $C_{10}HF_{11}$ requires C, 36·4; H, 0·3; F, 63·3%): M/e, 330(M): 230($M-C_2F_4$); 330(M); 261($M-CF_3$); 180($M-C_3F_6$); 280($M-CF_2$); 311(M-F); 161($M-C_3F_7$); 211($M-C_2F_5$); 223($M-CF_5$); 192($M-C_2F_6$); 123($M-C_3F_9$); 242($M-CF_4$).

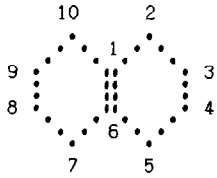
(10): 3H,4H,8H-Tridecafluorobicyclo[4,4,0]dec-1(6)-ene (nc); m.p. 54-56 °C; (Found: C, 31·4; H, 0·8; F, 67·8. $C_{10}H_3F_{13}$ requires C, 32·4; H, 0·8; F, 66·8%): M/e, 370(M): 288($M-C_2HF_3$); 113(C_3HF_4); 95($C_3H_2F_3$);

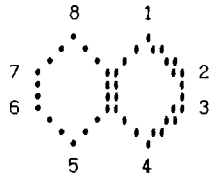
237($M-C_3H_2F_5$); 306($M-C_2H_2F_2$); 218($M-C_3H_2F_6$); 82(C_2HF_3); 219($M-C_3HF_6$); 199($M-C_3H_2F_7$); 351(M-F); 64($C_2H_2F_2$).

TABLE 1

NMR spectra of compounds 2 - 10

Measurements were done on neat liquids at 60 MHz for ^1H and at 56·4 MHz for ^{19}F, results being quoted in ppm, relative to, respectively, tetramethylsilane and trichlorofluoromethane.





b = broad, c = complex, d = doublet, m = multiplet, s = singlet, t = triplet

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
2	F	104·5	2	2, 5	cs
		111·7	2	7, 10	cs
		135·4	2	8, 9	c
		154·1	1	3, 4	c
3	H	5·15	(1)	3; >CHF	d of m; J_{HF} = 46·0
	F	98·2; 108·2	2	2	AB; J_{AB} = 317
		109·1; 116·4	2	5	AB; J_{AB} = 310
		109·2; 115·4	4	7, 10	AB; J_{AB} = 310
		127·2; 131·4	2	4	AB; J_{AB} = 297
		133·6; 137·7	4	8, 9	AB; J_{AB} = 280
		216·7	1	3; >CFH	d of m; J_{HF} = 46·0
4	H	5·15	(1)	8; >CHF	d of m; J_{HF} = 46·8
	F	98·0; 108·8	2	7	AB; J_{AB} = 305
		104·9	4	2, 5	cs
		110·7; 114·6	2	10	AB; J_{AB} = 302
		127·3; 131·5	2	9	AB; J_{AB} = 285
		154·1	2	3, 4	cd; J = 12·5
		217·3	1	8; >CFH	d of m; J_{HF} = 46.8

(continued)

TABLE 1 (cont.)

Compound Number		Chemical Shifts	Relative Intensity	Position in Formula	Type of Signal and Couplings
5	H	5·12	(1)	3, 4; >CHF	d of m; J_{HF} = 54·7
	F	106·4	2	2, 5	bs
		106·9; 118·2	2	7, 10	AB; J_{AB} = 308
		131·7; 139·8	2	8, 9	AB; J_{AB} = 275
		215·3	1	3, 4; >CFH	d of m; J_{HF} = 54·8
7 + 8	H	5·18	(2)	3, 8 and 3', 9'	d of m; J_{HF} = 46·8
	F	97·0; 108·8	2	2, 10	AB; J_{AB} = 310
		100·5; 110·0	2	2', 7'	AB; J_{AB} = 313
		113·2	2	5, 7	bs
		107·3; 118·9	2	5', 10'	AB; J_{AB} = 308
		126·2; 131·2	2	4, 8	cAB; J_{AB} = 276
		128·7; 131·7	2	4', 9'	cAB; J_{AB} = 282
		216·0	1	3,9; >CFH	d of m; J_{HF} = 43·9
		219·9	1	3',8'; >CFH	d of m; J_{HF} = 45.0
9	H	7·18	(1)	2	d of t; J = 6·7, 9
	F	105·5	4	5, 8	cm
		108·9	1	1	cm
		120·9	1	3	cm
		134·4	4	6, 7	bs
		138·3	1	4	cm
10	H	5·04	(3)	3, 4, 8; >CHF	d of m; J_{HF} = 49
	F	95·6; 110·4	2	7	AB; J_{AB} = 310
		104·7; 109·2	4	2, 5	AB; J_{AB} = 298
		104·0; 122·7	2	10	AB; J_{AB} = 320
		125·5; 131·6	2	9	AB; J_{AB} = 290
		213·2	1	8; >CFH	d of m; J_{HF} = 46
		216·1	2	3,4; >CFH	cd; J_{HF} = 48

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