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POLYFLUOROBICYCLO[4,4,0]DECANES. PART I.

THE FLUORINATION OF TETRALIN OVER COBALT TRIFLUORIDE

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SUMMARY

Fluorination of tetralin over cobalt trifluoride at 250<sup>0</sup> in a stirred reactor gave the known cis- and trans- perfluorodecalins and two known fluorobicyclo[4,4,0]dec-1(6)-enes. Also obtained were five new heptadecafluorobicyclo[4,4,0]decanes. Dehydrofluorinations of these gave five new hexadecafluorobicyclo[4,4,0]decenes of which one, the 1(2)- isomer, rearranged readily to the 1(6)- isomer.

INTRODUCTION

The fluorination of benzene with cobalt trifluoride under mild conditions has been studied extensively in this Department, and the structures and stereochemistry of the major products, polyfluorocyclohexanes, worked out in detail, as well as their dehydrofluorinations to give ranges of polyfluorinated cyclohexenes and -dienes, and benzenes [1]. Tetralin had been fluorinated earlier [2] at 320 - 340<sup>0</sup> to give a good yield of perfluorodecalin, later [3] separated into the cis- and trans- isomers. The present work was carried out in 1969-70, and involved the fluorination of tetralin at lower temperatures (ca 250<sup>0</sup>). It was carried out concomitantly with the already reported [4] fluorination of tetralin and naphthalene over potassium tetrafluorocobaltate [5] and was referred to briefly therein, and has also been cited by our colleagues [6], in their development of the cation-radical theory of fluorination.

## RESULTS AND DISCUSSION

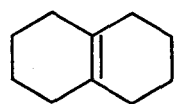
Tetralin was fluorinated smoothly at 250° to give a good recovery of product (2.3×weight of starting material). Distillation, followed by gas chromatography, gave nine compounds (A - I), of which four were identical with known products. Compound A had been made first from the octafluoronaphthalene/CoF<sub>3</sub> reaction [7], and subsequently from naphthalene/KCoF<sub>4</sub> [4], and from naphthalene, tetralin, or decalin/CsCoF<sub>4</sub> [8]. Compounds B and C came from tetralin/CoF<sub>3</sub> [3], and H from naphthalene or tetralin/KCoF<sub>4</sub> [4].

The remaining five new compounds (D,E,F,G and I) were all shown by analysis to be heptadecafluorobicyclo[4,4,0]decanes (C<sub>10</sub> H F<sub>17</sub>). Their structures were studied by dehydrofluorination, and from their spectroscopic parameters. The earlier investigations on polyfluorocyclohexanes [9] suggested that all possible olefinic products would be formed in each case by treatment with aqueous potassium hydroxide. Further, stereoisomeric polyfluorocyclohexanes which dehydrofluorinated most readily were those with an isolated axial hydrogen and an adjacent axial fluorine (antiperiplanar) as opposed to those with an isolated equatorial hydrogen.

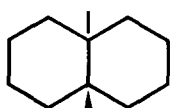
Two of the C<sub>10</sub> H F<sub>17</sub> compounds (G and I) each reacted with aqueous potassium hydroxide to give the same two olefins, (J and K). Both had formula C<sub>10</sub>F<sub>16</sub>, and infrared C=C bands at 1760 (J) and 1780 cm<sup>-1</sup> (K) indicated that they had CF=CF groups. Hence, G and I were stereoisomers, with identical ring fusion, but differing orientations of H at position 3 (see Scheme).

A third C<sub>10</sub> H F<sub>17</sub> compound (F) also gave two olefins on dehydrofluorination, but these (L and M) differed from J and K. However, they also had CF=CF groups, showing infrared bands at 1740 (L), and 1770 cm<sup>-1</sup> (M). Compound F therefore had different ring fusion from G and I, but also had H in position 3.

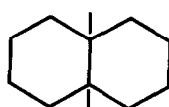
Perfluoro-trans-decalin (B) has a strong infrared band at 760 cm<sup>-1</sup>, where perfluoro-cis-decalin (C) has only a weak band: C has strong bands at 820 and 862 cm<sup>-1</sup>, where B has only weak bands. The strongest



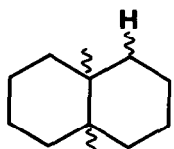
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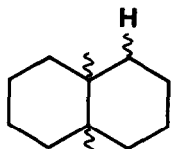
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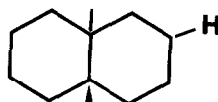
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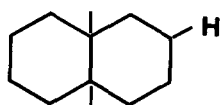
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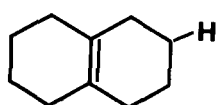
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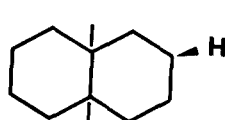
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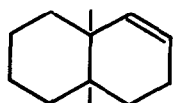
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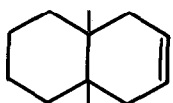
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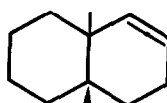
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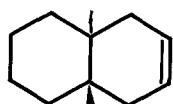
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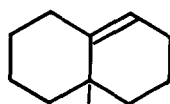
K



L



M



N

all unmarked bonds are to  
fluorine

S C H E M E

infrared bands, in this general region, present in the spectra of the new compounds were as follows:-

G, 810, 820, 830, 860; I, 810, 815, 822; J, 810, 835, 860; K, 835; F, 750; L, 785; M, 785  $\text{cm}^{-1}$ . Thus, G and I had 3H-cis-decalin structures, whilst F was a 3H-trans-decalin.

Nmr parameters for the compounds made are listed in Table 1. Those for the 1 and 6 tertiary fluorine positions did not help much with structural assignments, but the peaks present in the  $\text{CF}_2$  region were broader for the cis-decalins (flipping) whereas the  $\text{CF}_2$  signals in the trans-decalins were sharper (rigid) as in the parent fluorocarbons (see Table 1), and confirmed the allocations based on infrared. Further, olefin M had a less complex nmr spectrum than had L and the tertiary F signal was sharper. Likewise K had a less complex nmr spectrum than had J; in this case J showed 2 tertiary fluorine peaks whereas K had only one. Thus K and M were the more symmetrical 3(4) enes and had respectively cis and trans ring fusions and J and L were the 2(3) enes, with respectively cis and trans ring fusions.

The stereochemistry of the 3H-substituents in F, G and I was suggested by detailed analysis of nmr data [10] as cis-3H-trans (F), cis-3H-cis (G), and trans-3H-cis (I).

Rates of dehydrofluorination of G and I did not differ very much, though a competition experiment indicated that G reacted marginally the faster. Also, G gave a slight predominance of olefin J, whilst I gave a little more of K. Since the ring forms of cis-decalins can interconvert, G and I should not show significant differences on dehydrofluorination: each will have a conformer with axial hydrogen. Trans-fused decalins are rigid, but compound F has an axial hydrogen, and so should dehydrofluorinate readily. In fact it reacted at much the same rate as G and I to give both trans-fused olefins with the more symmetrical one (M) predominating.

The two remaining heptadecafluorides (D and E) were present in the smallest quantities and were difficult to obtain pure. Dehydrofluorinations on each apparently gave two sets of three olefinic products. The first one from each was easily shown to be the same bicyclic olefin (A) as that obtained earlier in the work. The third product (N) was also the same from each set and was found to be labile. Use of more dilute alkali in the dehydrofluorination of a mixture of

D and E increased the proportion of it in the product at the expense of A, whereas more forcing conditions gave no compound N at all, only A + the third product. Isolation of N was accomplished by glc, and it was another  $C_{10}F_{16}$  isomer. There was a strong C=C absorption in the infrared at  $1700\text{ cm}^{-1}$  (cf. compound A which has no detectable C=C band in the infrared) and only one tertiary fluorine in the nmr spectrum.

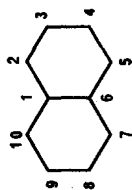
Hence N was hexadecafluorobicyclo[4,4,0]dec-1(2)-ene. With potassium fluoride in dimethylformamide, it was entirely converted to A. It seems certain therefore that A was not formed in the dehydrofluorination reaction directly, but arose by rearrangement of N due to the increasing presence of fluoride ion as the dehydrofluorination proceeded. The presence in N but not in A of a vinylic fluorine (I -  $\pi$  effect) and of an allylic tertiary fluorine (probably relatively unstable), are presumably reinforced by stereochemical factors in rendering the former so much less stable than the latter. There was a third olefin present in the dehydrofluorination products of D and E, and glc indicated that it was L or J. It was however a minor component and sufficient for positive identification could only be obtained from a mixture of D + E. The product thus obtained was identified by infrared and nmr as a mixture of J and L, with the latter slightly in excess.

It was thus clear that D and E both had 2H- substituents, and their infrared and nmr spectra indicated that each was probably fairly pure. Unfortunately, in the infrared spectrum of D, strong bands were present at 785 and 815, and, strongest of all, at  $825\text{ cm}^{-1}$ , whilst for E there were strong bands at 750 and 775, but a medium band at  $820\text{ cm}^{-1}$ . It seems likely that D was a cis ring-fused decalin and E was a trans ring-fused decalin, but an unequivocal allocation of structure is not possible at the present time.

There is special interest in D and E since they are the first cyclohexane compounds in which an isolated tertiary fluorine competes with one from a  $CF_2$  group to be eliminated in dehydrofluorination. In fact, the tertiary fluorine was lost preferentially from both D and E (the proportions A + N : L varied between 10 : 1 and 12 : 1). The relative rates of consumption of D and E from the mixture were not very different in a competition experiment (D reacted slightly faster).

TABLE 1

$^{19}\text{F}$  Nmr Spectra of Bicyclo[4,4,0]dec-anes and -enes



Formula	Ring Position									
	1	2	3	4	5	6	7	8	9	10
<b>Saturated</b>										
B trans perfluoro*	189.3bs	189.3bs	115.3	142.8	142.8	(2 overlapping ABs)				
C cis perfluoro*	189.0s	189.0s	122.8	131.6	131.6	(2 broad singlets)				
D 2H-	206.3s	198.3s	229.8t	104.4	144.6	(overlapping ABs)				
E 2H-	195.3bs	184.1bs	228.5t	105.4	142.5	(overlapping ABs)				
F cis-3H-trans	187.3s	184.0s	234.7d	105.2	140.1	(overlapping ABs)				
G cis-3H-cis	194.9s	192.6s	233.1bs	113.5	131.3	broad peaks				
I trans-3H-cis	191.3s	189.2s	232.7bd	113.1	141.7	broad peaks				
<b>Mono-enes</b>										
A 1(6) ene	-	-	108.7, 131.3	(2 sharp singlets)						
H 3H-1(6)ene	-	-	219.3bs	96.9	141.7					
J cis-2(3)ene	191.9s	182.3s	112.5	150.3						
K cis-3(4)ene	190.7s	190.7s	104.1	135.9						
L trans-2(3)ene	182.0bs	182.0bs	164.5bs	105.5	146.3					
M trans-3(4)ene	201.2s	201.2s	174.4s	174.4s	126.3	163.9	sharp peaks			
N 1(2)ene	-	164.7s	95.7	146.0						

\*Measurements done on a Perkin Elmer R10 machine at 56.4 MHz.

s = sharp singlet

bs = broad singlet

d = doublet

bd = broad doublet

t = triplet

Further work on these and related polyfluorodecalins has now been started since a number of interesting issues have been raised, but not sorted out, in this study

## EXPERIMENTAL

Gas-liquid chromatography (glc). Some analytical work was done in a Pye 104 machine using 9.1m capillary columns coated with UCON LB 550. Other analyses were done on a Pye 105 machine using columns 9.1m x 9.5mm packed with 20% dinonyl phthalate/chromosorb (DNP) or 20% UCON LB 550 on chromosorb (UCON). Temperature and nitrogen overpressure are given in each case. Preparative separations were done on the Pye 105 machine by repeated injections onto columns 9.1m x 9.5mm, or on 5m x 35mm columns. Proportions are calculated from peak areas (based on peak height x width at  $\frac{1}{2}$  height).

Spectroscopy. Infrared (ir) spectra were recorded either on a Pye Unicam SP 200G instrument or on a Perkin Elmer 257 instrument as thin liquid films on sodium chloride plates.

Nuclear magnetic resonance (nmr) was done on a Varian HA 100 spectrometer at 94.1 MHz unless otherwise stated, measurements being done on neat liquids. Results quoted are in ppm relative to trichlorofluoromethane used as internal reference, and are negative.

Mass spectra were measured on an A.E.I. MS9 instrument.

Fluorination of Tetralin. A standard stirred reactor [11] was used containing cobalt trifluoride (10 kg), and run at 250<sup>o</sup>. In a typical run, tetralin (150g) in a stream of nitrogen (20 l/h) was passed into the reactor during 3h, the product being collected in a trap cooled in solid CO<sub>2</sub>. The nitrogen flow was continued for 1h further, and the trap contents washed with water, sodium bicarbonate solution, water again, and dried (P<sub>2</sub>O<sub>5</sub>) to give crude product (355g).

Simple distillation of such product (973g) gave two cuts, b.r. 110 - 170<sup>o</sup> (792g) and b.r. > 170<sup>o</sup> (180g). The first cut was analysed by glc (UCON capillary column at 30<sup>o</sup>, 15 psi) and showed peaks corresponding to 9 products in the following ratios to peak F (the largest):- A, 0.21: B, 0.98: C, 0.81: D, 0.10: E, 0.15:

F, 1: G, 0.33: H, 0.43: I, 0.45. Apart from 5 very small peaks (area negligible) of short retention time close by the peak from A, there was nothing else of significance running before I. There were 6 peaks after I, (ratios to F: 0.04, 0.15, 0.27, 0.03, 0.07, 0.09) which were not investigated further.

The cut b.r. 110 - 170<sup>0</sup> (700g) was fractionally distilled through a 4 ft. vacuum-jacketed column packed with Dixon gauzes and at a reflux ratio of 60:1 to give 3 fractions: (i) b.r. 110 - 130<sup>0</sup> (14.5g), (ii) b.r. 130 - 144<sup>0</sup> (117g) and (iii) b.r. 144 - 160<sup>0</sup> (257g).

Isolation of Fluorination Products. Fraction (i) by glc analysis (UCON, 70<sup>0</sup>, 20 psi) contained 2 very minor and 3 trace short retained peaks and A, B, C and H in the ratios to A, 1 : 0.16 : 0.06 : 0.08, respectively. Isolation by preparative glc gave hexadecafluoro-bicyclo[4,4,0]dec-1(6)-ene (A) b.p. 126<sup>0</sup> [4,7,8]; perfluoro-trans-decalin (B) b.p. 141<sup>0</sup>, ir 760(s), 820(w), 850(w) cm<sup>-1</sup> [3]; perfluoro-cis-decalin (C) b.p. 142<sup>0</sup>, ir 760 (vw), 820 (vs), 862 (s) cm<sup>-1</sup> [3]; all identified by ir. Fraction (ii) by similar glc analysis contained the same products A, B, C, H in respective proportions 0.05 : 1 : 0.47 : 0.38. On a preparative scale (5g in a 5m x 35mm column, DNP/chromosorb 20% at 90<sup>0</sup>, N<sub>2</sub> 20 l/h) 3H-pentadecafluorobicyclo[4,4,0]dec-1(6)-ene (H), b.p. 138<sup>0</sup>, ir 2980 cm<sup>-1</sup> (C - H) was isolated and identified by ir [4]. Fraction (iii) on glc analysis (UCON, 80<sup>0</sup>, 20 psi) gave 14 peaks in proportions B, 0.08: C, 0.18: D, 0.09: E, 0.14: F, 1.0: G, 0.41: H, 0.01: I, 0.47 : unknowns; 0.04, 0.21, 0.32, 0.04, 0.06, 0.04. Preliminary preparative scale separation on a 5m x 35mm column packed with DNP/chromosorb 20% at 85<sup>0</sup>, N<sub>2</sub> 20 l/h was done in 7 batches and gave D + E, F, and G + I. Each product was further purified by the Pye 105 machine. These were obtained by glc (UCON) (a) 2H-heptadecafluorobicyclo[4,4,0]decane (D), nc, b.p. 148<sup>0</sup> (Found: C, 26.9; F, 72.5%. M 443.980. C<sub>10</sub>H<sub>F</sub><sub>17</sub> requires C, 27.0; F, 72.7%. M, 443.981); ir 2995 (C-H) 785(s), 815(s), 825(vs), 840(w), 850(w) cm<sup>-1</sup>: (b) 2H-heptadecafluorobicyclo[4,4,0]decane (E) nc, b.p. 148<sup>0</sup> (Found: C, 26.8; F, 73.0%. M, 443.981); ir 2980 (C - H) 750 (s), 775 (s), 820 (m), 850 (w) cm<sup>-1</sup>. Glc (DNP) gave (c) cis-3H-heptadecafluoro-trans-bicyclo[4,4,0]decane (F), nc, b.p. 150<sup>0</sup> (Found: C, 26.8; F, 72.5%. M-19, 424.976. C<sub>10</sub>H<sub>F</sub><sub>17</sub> requires M-19 424.982); ir 2980 (CH), 750 (vs), 775 (w) 790(w), 810 (w), 830 (m), 840 (m) cm<sup>-1</sup>.



Glc (UCON) gave (d) cis-3H-heptadecafluoro-cis-bicyclo[4,4,0]decane (G),  
nc, b.p. 151<sup>o</sup> (Found: C, 27.2; F, 72.5%. M-19, 425); ir 2980 (CH),  
730 (w), 810 (s), 820 (s), 830 (m), 860 (m) cm<sup>-1</sup>; and also  
(e) trans-3H-heptadecafluoro-cis-bicyclo[4,4,0]decane (I) nc,  
(Found: C, 26.7; F, 73.0%. M-19, 425); ir 2980 (C H), 750 (vw),  
810 (m), 815 (m), 822 (s), 850 (w) cm<sup>-1</sup>.

#### Dehydrofluorinations of Heptadecafluorobicyclo[4,4,0]decanes.

##### General method

Each compound, in quantities of 1 - 2g, was shaken with aqueous potassium hydroxide. Recorded for each experiment are the proportions (fluorohydrocarbon: KOH : H<sub>2</sub>O), reaction temperature (<sup>o</sup>C) and time (min). Weight recoveries of products were 80-90%, and proportions present were determined by glc analysis on a Pye 104 chromatograph (column, temperature, and nitrogen overpressure given in each case). Products were isolated by the Pye 105 machine used preparatively with similar conditions.

(i) trans-3H-cis-isomer (I) Reactant proportions 1:10:10 at 15<sup>o</sup> for 3 min : glc, UCON at 76<sup>o</sup> and 23 psi, showed that present were compounds J and K and starting material (I) in the ratio 0.71:1.0:0.3.

Isolation (glc) gave hexadecafluoro-cis-bicyclo[4,4,0]dec-2(3)-ene (J), nc (Found: C, 28.6; F, 71.7. C<sub>10</sub>F<sub>16</sub> requires C, 28.3; F, 71.7%); ir 1760 (s, C=C), 810 (m) 835 (s), 860 (m) cm<sup>-1</sup>. ; and hexadecafluoro-cis-bicyclo[4,4,0]dec-3(4)-ene (K),nc (Found: C, 28.0; F, 71.7%); ir 1780 (s, C=C), 825 (w), 840 (s), 875 (m) cm<sup>-1</sup>.

(ii) Cis-3H-cis-isomer (G) Reaction conditions as in (i) above: glc, DNP at 92<sup>o</sup> and 27 psi showed the presence of J, K and G in the ratio 1.0 : 0.53 : 0.12.

(iii) Mixture of G and I G + I (0.60: 1.0), conditions as in (i) above gave J, K, G and I, in proportions 1.0:0.98:0.10:0.30.

(iv) Cis-3H-trans-isomer (F) (a) Reactant proportions 1:10:10 at 15<sup>o</sup> for 3 min: glc, DNP at 92<sup>o</sup> and 27 psi showed 3 peaks due to L, M and F in proportions 0.53: 1.0:0.41. (b) Reactant proportions 1:1:1 at 100<sup>o</sup> for 60 min: glc analysis as before gave only L and M in ratio 0.37:1.0. Isolation by glc gave hexadecafluoro-trans-bicyclo[4,4,0]dec-2(3)-ene (L), nc (Found: C, 28.5; F, 71.9%; M, 424); ir 1740 (s, C=C), 785 (s), 805 (w) cm<sup>-1</sup>; and

hexadecafluoro-trans-bicyclo[4,4,0]dec-3(4)-ene (M), nc  
(Found: C, 28.1; F, 71.6%; M, 424); ir 1770 (s, C=C), 785 (s)  $\text{cm}^{-1}$ .

(v) 2H-isomer (D) Reactant proportions 1:10:10 at 15<sup>0</sup> for 2 min: glc, DNP at 93<sup>0</sup> and 27.5 psi showed 4 peaks due to A, N, L or J and D in proportions 0.44: 0.40: 0.08: 1.0.

(vi) 2H-isomer (E) Conditions and products as in (v) above: proportions A : N : L or J : E = 0.22 : 0.26 : 0.04 : 1.0.

(vii) Mixture of D + E (0.74 : 1.0)

(a) Reactant proportions 1 : 10 : 10 at 15<sup>0</sup> for 1 min: glc, DNP at 94<sup>0</sup> and 28 psi gave proportions A : N : L + J : D : E = 0.45 : 0.26 : 0.07 : 0.68 : 1.0. Reaction for 3 min gave proportions A : N : L + J : D + E = 1.0 : 0.62 : 0.21 : 0.51 : 0.86, with D : E ratio 0.59 : 1.0.

(b) Reactant proportions 1 : 1 : 1 at 100<sup>0</sup> for 45 min : glc, DNP at 68<sup>0</sup> and 18 psi showed only 2 peaks corresponding to A and L + J in proportion 1.0 : 0.12.

(c) Reactant proportions 1 : 10 : 25 at 15<sup>0</sup> for 2 min followed by glc as in (v) showed proportions A : N : L + J : D : E = 0.14 : 0.46 : 0.02 : 0.44 : 1.0.

The identity of A was suggested by glc as hexadecafluorobicyclo-[4,4,0]dec-1(6)-ene and confirmed by ir and ms identity with authentic specimens, and the sample above from the fluorination.

Hexadecafluorobicyclo[4,4,0]dec-1(2)-ene (N), nc, was isolated pure from run viic (Found: M, 424) ir 1700 (s, C=C)  $\text{cm}^{-1}$ .

When N (0.5g) was shaken with anhydrous potassium fluoride (0.5g) in dimethylformamide (2  $\text{cm}^3$ ) at 15<sup>0</sup> for 16h there was quantitative conversion to A.

A sample of the 2(3)-ene was isolated from experiments (vii) above and was shown by ir and nmr to be a mixture of J + L with the latter in slight excess.

#### ACKNOWLEDGEMENTS

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