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FLUOROC*YCLO*HEXANES—II*

CIS- AND *TRANS*- 1H:3H- AND 1H:4H-DECAFLUOROC*YCLO*HEXANES†

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Abstract—An extension of the methods employed in the isolation of (*trans*) 1H/2H-decafluoro*cyclo*hexane,[1] (I) from the polyfluoro*cyclo*hexane mixture obtained by the vapour phase fluorination of benzene with cobaltic fluoride at about 150°, has afforded the four remaining members of the series of decafluoro*cyclo*hexanes [the *cis*- and *trans*- 1H:3H- and 1H:4H-isomers (1H:3H/-(IV), 1H/3H-(III), 1H:4H/-(VII), and 1H/4H-(VIII), respectively)] and also the *cis*-1H:2H-decafluoro*cyclo*hexane (II), obtained previously[1,2] by the lithium aluminium hydride reduction of 1:2-dichlorodecafluoro*cyclo*hexane. The structures of the 1H:3H- and 1H:4H-decafluorides have been established by dehydrofluorination studies. The six decafluoro*cyclo*hexanes have been related to two new nonafluoro*cyclo*hexanes[3] (IX and X) by further fluorination of the latter. 2H-Heptafluoroadipic acid has been obtained from 3H-nonafluoro*cyclo*hex-1-ene (V), one of the dehydrofluorination products of the 1H:3H-decafluorides.

BY the passage of benzene in the vapour phase over cobaltic fluoride at about 150° a complex mixture of polyfluoro*cyclo*hexanes has been obtained.[1] This may be separated by fractional distillation controlled by analytical gas chromatography,[1,4] and pure fluorohydrocarbons isolated. The lowest boiling members, undecafluoro*cyclo*hexane[5,6] and 1H/2H-decafluoro*cyclo*hexane[1] (I) have been described already. The 1H:2H/-decafluoride (II) has also been made by a different method[2] and its structure proved.[1] In the present paper and the following one,[3] the characterisation of some higher-boiling components of the polyfluoro*cyclo*hexane mixture is described. In the first paper of this series[1] the results of a gas chromatographic analysis of this mixture were given in tabular form; the compounds to be described here gave peaks numbered 5, 6, 8 and 9.

*Isolation of decafluoro*cyclo*hexanes*

Further fractional distillation of the polyfluoro*cyclo*hexane mixture, obtained as before, gave, after removal of material boiling below 70°, a major fraction having b.p. 78° (peak 5). This had been investigated before[6,7,8] and was thought to be a pure compound, since it gave a single peak in analytical gas chromatography[8] using a dinonyl phthalate/kieselguhr packing (the only one available when the work was done).

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* Part I was published in *J. Chem. Soc.* 2505 (1957).

† The nomenclature used is based on that suggested for hydroxy*cyclo*hexanes S. J. Angyal and C. G. Macdonald *J. Chem. Soc.* 686 (1952); D. H. Whiffen *Chem. & Ind.* (*Rev.*) 964 (1956).

[1] R. P. Smith and J. C. Tatlow *J. Chem. Soc.* 2505 (1957).

[2] J. Roylance, J. C. Tatlow and R. E. Worthington *J. Chem. Soc.* 4426 (1954).

[3] J. A. Godsell, M. Stacey and J. C. Tatlow *Tetrahedron* **2**, 193 (1958).

[4] D. E. M. Evans and J. C. Tatlow *Vapour Phase Chromatography* (Edited by D. H. Desty) p. 256. Butterworths, London (1956).

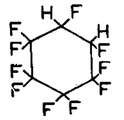
[5] J. C. Tatlow and R. E. Worthington *J. Chem. Soc.* 1251 (1952).

[6] A. K. Barbour, H. D. Mackenzie, M. Stacey and J. C. Tatlow *J. Appl. Chem.* **4**, 341, 347 (1954).

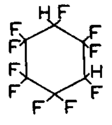
[7] D. E. M. Evans and J. C. Tatlow *J. Chem. Soc.* 3779 (1954).

[8] D. E. M. Evans and J. C. Tatlow *J. Chem. Soc.* 1184 (1955).

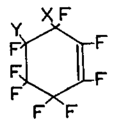
A 1H:3H-structure (III or IV) was then assigned to the compound, since dehydrofluorination[7,8] afforded octafluoro*cyclo*hexa-1:4- and -1:3-diene and 3H-(V) and 4*H*-nonafluoro*cyclo*hex-1-ene (VI). However, later investigations on gas chromatography[4] showed that, on other packings, notably silicone oil/silicone rubber, the fraction (5), b.p. 78°, was resolved into two components. For various reasons, at that time, preparative-scale gas chromatography tubes could not be operated with any of the packings which resolved the mixture. A partial separation of it was obtained by careful refractionation of the two intermediate mixtures having b.r. 71–78° and b.r. 79–85°, followed by separation of two subfractions obtained (b.r. 72–74° and 80–81° respectively) by preparative-scale gas chromatography over dinonyl phthalate/kieselguhr. This removed, respectively, the 1H/2H-decafluoride (I) b.p. 70°, and the decafluoride (6) b.p. 86° (see later), leaving two samples, one considerably enriched in the lower-boiling (5A) and the other in the higher-boiling (5B) component of the fraction of b.p. 78°. Preliminary investigations were carried out on these incompletely pure specimens. Later, an almost complete separation of the two components of fraction (5) (b.p. 78°) was achieved by a direct application of preparative-scale gas chromatography using a column packing of tricresyl phosphate/kieselguhr (1:3); the lower boiling isomer (5A) containing about 9 per cent of the higher one, the latter (5B) being obtained pure.



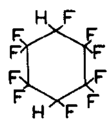
I 1Ha/2Ha (trans)
II 1Ha:2He/(cis)



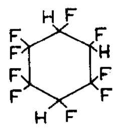
III 1 Ha/3He (trans)
IV 1 Ha: 3 Ha/(cis)



V X =H, Y= F
VI X =F, Y=H



VII 1Ha: 4 He/(cis)
VIII 1Ha/4 Ha (trans)



IX 1Ha: 4He/2Ha
X 1 Ha/2 Ha: 4 Ha

In another aspect of the present investigation (see later), two stereoisomeric nonafluoro*cyclo*hexanes were further fluorinated by cobaltic fluoride. *Inter alia*, compound (5A) free from (5B) was obtained from one nonafluoride, and compound (5B) free from (5A) from the other. Each was separated readily from the other products of fluorination by preparative-scale gas chromatography over dinonyl phthalate/kieselguhr, and was thus obtained completely pure. It was shown by infrared spectroscopy that the major component of the impure samples of compound (5A) was the same as this pure specimen, and likewise for compound (5B). Also, the original fraction (5), b.p. 78°, contained only the two components (5A) and (5B).

Fractional distillation of the polyfluoride mixture having boiling point greater than 79° gave a major fraction (peak 6[1]), b.p. 86°, which could not be resolved further by any available analytical gas chromatography packings and was pure.

Analytical gas chromatography[1] had shown that there were three compounds having boiling points near to 90°. One, a large fraction (peak 7), b.p. 92° is a nonafluoro*cyclo*hexane and is described in a later paper.[3] The other two were small components (peaks 8 and 9) and they could not be separated by distillation, since all fractions boiling between 86° and 92° contained compounds 6, 7, 8 and 9. Accordingly, a fraction was taken with maximum concentrations of the new compounds, and separated by preparative-scale gas chromatography to give the two pure compounds (8) and (9). These had boiling points of 91° and 89° respectively, and it is of interest that in the series of three compounds (7, 8 and 9) the gas chromatographic retention times on a packing of dinonyl phthalate/kieselguhr are in the reverse order of boiling point.

*Dehydrofluorination studies on the decafluoro*cyclo*hexanes*

All of the compounds (5A, 5B, 6, 8 and 9) isolated as described above were shown by analysis to be decafluoro*cyclo*hexanes. Compound 8 (b.p. 91°) had a gas chromatographic retention time identical with that of the known 1H:2H/-decafluoro*cyclo*hexane[1,2] (II), and comparison of the infra-red spectra confirmed the identification.

The other four compounds were investigated by dehydrofluorination with aqueous potassium hydroxide. Compounds (5A) and (6) afforded three products, as shown by analytical gas chromatography, with retention times the same as those of octafluoro*cyclo*hexa-1:4- and -1:3-diene and 4H-nonafluoro*cyclo*hex-1-ene (VI). No 3H-olefin (V) could be detected, however. Compounds (5B) and (9) gave four products, shown by analytical gas chromatography to be the two dienes mentioned above, and both the 3H- and the 4H-mono-olefins (V) and (VI). The identity of all of these olefins was proved conclusively by the separation of each of the four products into its components using preparative-scale gas chromatography, followed by comparisons of their infra-red spectra with those of known samples.[7,8] Also, the three olefins derived from compound (6) (b.p. 86°), the first to be investigated, were oxidised to give dibasic acids, difluoromalonic acid from the 1:4-diene, tetrafluorosuccinic from the 1:3-diene, and 3H-heptafluoroadipic from the 4H-olefin (VI).

The oxidation of the 3H-olefin (V) to give the derived dicarboxylic acid had been attended by experimental difficulty in the earlier work,[8] the acid and its derivatives being of doubtful purity. Accordingly, this process was re-examined. If the olefin was treated at about 70° with aqueous potassium permanganate containing sodium bicarbonate the primary product, 2H-heptafluoroadipic acid was obtained in good yield and it could be purified fairly readily. It was characterised as the free acid, dianilinium salt, and di-(S-benzylthiuronium) salt. The 2H-acid itself, as expected, was less stable than its 3H-isomer; fluoride ion was eliminated more readily on reaction with aqueous bases. However, it may be handled without unusual difficulty when pure and is fairly stable to heat. With aqueous permanganate at 100°, the 2H-acid was degraded, some tetrafluorosuccinic acid was formed as well as the hexafluoroglutaric acid reported earlier.[8] The 3H-olefin (V), with aqueous potassium permanganate at 100°, gave hexafluoroglutaric acid as reported before.[8] The samples of the derivatives of 2H-heptafluoroadipic acid obtained previously were essentially correct, but as suspected were contaminated with material from the breakdown of the olefin (V) and the 2H-acid itself arising because the oxidation was too vigorous.

*Structures of the decafluoro*cyclo*hexanes*

Identification of the products obtained by dehydrofluorination of the decafluoro*cyclo*hexanes showed clearly that compounds (5A) and (6) which afforded no 3H-olefin (V) were 1H:4H-decafluorides (VII and VIII), whilst the other two (5B) and (9), which gave the 3H-olefin, were 1H:3H-compounds (III) and (IV). Preliminary indications of the stereochemistry of each compound were obtained by qualitative comparisons of the rates of dehydrofluorination. Assuming that the dehydrofluorination mechanisms discussed in Part I of the series[1] apply here, then, for the preferred process to operate, the groups to be eliminated, hydrogen and fluorine, must both occupy axial positions. With 1H:3H- and 1H:4H-decafluorides there is always an axial fluorine substituent available on either side of a $>$CHF group in all possible conformations. If, as seems certain in the decafluoride series, the more stable conformations are those in which the small hydrogen substituents are carried where possible in axial positions, there should be two isomers with two axial hydrogen atoms and two with one axial and one equatorial hydrogen. The first two isomers should be dehydrofluorinated more readily than those with only one axial hydrogen, since both positions are available for attack by the base at the outset in the orientations required for the easiest elimination process to operate. In a series of comparative dehydrofluorination experiments (see Table) it was found that, under mild conditions, the 1H:4H-compound (6) (b.p. 86°) gave some of the 4H-olefin (VI) but no detectable amounts of either the octafluoro*cyclo*hexa-1:4- or -1:3-diene, whereas the stereoisomeric 1H:4H-compound (5A) gave readily detectable amounts of all these compounds. Likewise, with the 1H:3H-pair, the stereoisomer of b.p. 89° (compound 9) gave readily detectable amounts of the dienes and the mono-enes (V and VI), whereas the other compound (5B) gave mono-enes but no dienes. Correspondingly, when more vigorous reaction conditions were used, complete dehydrofluorination of all of the starting material occurred with compounds (5A) and (9), whereas appreciable amounts of the decafluoro*cyclo*hexanes remained with the other

TABLE 1. COMPARATIVE DEHYDROFLUORINATIONS OF DECAFLUORO*cyclo*HEXANES

Decafluoro*cyclo*hexane under test			Dehydrofluorination reactions					
Fraction no.	Structure	b.p. (°C)	Conditions used	Relative peak sizes given by products				
				1:4-C_6F_8	1:3-C_6F_8	4H-C_6HF_9	3H-C_6HF_9	Starting material
6	1H:4H/-	86	A	*a*	*a*	*vw*	*a*	*vs*
5A	1H/4H-	78	A	*vw*	*vw*	*m*	*a*	*vs*
9	1H:3H/-	89	A	*vw*	*vw*	*w*	*w*	*vs*
5B	1H/3H-	78	A	*a*	*a*	*vw*	*vw*	*vs*
6	1H:4H/-	86	B	*m*	*m*	*vs*	*a*	*m*
5A	1H/4H-	78	B	*s*	*s*	*s*	*a*	*a*
9	1H:3H/-	89	B	*s*	*s*	*vs*	*s*	*a*
5B	1H/3H-	78	B	*s*	*m*	*s*	*s*	*m*

a = absent, *vw* = very weak, *w* = weak, *m* = medium, *s* = strong, *vs* = very strong.

pair, (5B) and (6). These results suggested strongly that compound (6), b.p. 86°, and the higher boiling component of the fraction of b.p. 78–79° (compound 5B) possess an equatorial hydrogen atom, i.e. they may be designated 1Ha:4He/- and 1Ha/3He-decafluoro*cyclo*hexane, respectively. The remaining two decafluorides possess di-axial hydrogen systems, i.e. the lower boiling component of the fraction b.p. 78–79° (compound 5A) is the 1Ha/4Ha-decafluoro*cyclo*hexane and compound (9), b.p. 89°, is the 1Ha:3Ha/-isomer.

These allocations of structure and those of the 1H:2H-compounds[1] could be tested by relating the decafluoro*cyclo*hexanes to two nonafluoro*cyclo*hexanes also obtained[3] from the polyfluoro*cyclo*hexane mixture. The nonafluorides were shown[3] by identification of dehydrofluorination products to be 1H:2H:4H-compounds; resolution of a derived 3H:4H-hexafluoroadipic acid in which the hydrogens retained the configuration of the original 1H:2H-system showed that both hydrogens of this were axial, i.e. *trans*, and rates of dehydrofluorination of the two isomers indicated that the lower-boiling one (b.p. 92°) was the 1Ha:4He/2Ha-compound (IX) and the other, b.p. 101°, was the 1Ha/2Ha:4Ha-stereoisomer (X).

These nonafluorides were fluorinated further by passage in the vapour phase over cobaltic fluoride in a small tubular static reactor. The nonafluoride (IX) gave five products, perfluoro*cyclo*hexane, undecafluoro*cyclo*hexane, and three decafluorides, the isomers 1Ha/2Ha- (I), b.p. 70°, 1Ha/3He-, (III), b.p. 78°, and 1Ha:4He/-(VII), b.p. 86°. Likewise, the nonafluoride (X) gave five products, perfluoro*cyclo*hexane, undecafluoro*cyclo*hexane, and three decafluorides, the isomers 1Ha/2Ha- (I), b.p. 70°, 1Ha:3Ha/- (IV), b.p. 89°, and 1Ha/4Ha- (VIII), b.p. 78°. Thus, the structures of the two series of compounds, deca- and nona-fluorides, arrived at independently, were related conclusively.

Infra-red measurements[9] of the C—H stretching frequencies of the six decafluorides also supported the stereochemical allocations made above. Final confirmation for the 1H:4H-decafluoro*cyclo*hexanes was obtained by measurements of the dipole moments of both isomers in benzene solutions. The observed dipole moments were: 1Ha/4Ha-decafluoro*cyclo*hexane (VIII) (b.p. 78°) 1·05 D (the accuracy of this determination was not high, but the true value could not exceed 1·5 D); 1Ha:4He/-decafluoro*cyclo*-hexane (VII) (b.p. 86°), 2·59D. Although these values, particularly the former, are only approximate, they demonstrate unequivocally the stereochemical configuration of each isomer, the *cis*-compound (VII), b.p. 86° possessing the larger dipole (2·59D) with which the calculated value (2·69D) is in good agreement. The lower boiling isomer (VIII) must therefore be the *trans*-compound.

All six decafluoro*cyclo*hexanes have thus been isolated and characterised conclusively. The structures, all suggested by dehydrofluorination reactions, are supported firmly by infra-red studies, and by dipole moments for the 1H:2H- and 1H:4H-pairs. Through the syntheses from the nonafluorides (IX and X), the 1H:3H-pair are related to all of these. The resolution of the acid derived from the nonafluorides (IX and X) is yet more proof of the structures of the 1H:2H-compounds. It must be noted that the fraction of b.p. 78° studied previously [6,7,8] was a mixture of the 1H/4H- and 1H/3H-isomers, which could not have been separated by the techniques then available. However, the products obtained by dehydrofluorination[7,8] were of course, pure, since the same olefins are derived from each. The decafluoro*cyclo*hexane mixture obtained[2]

[9] D. Steele and D. H. Whiffen *Tetrahedron* In press (1958).

by lithium aluminium hydride reduction of the mixed dichlorodecafluoro*cyclo*hexane isomers formed[5] by fluorination of *o*-dichlorobenzene has been examined by gas chromatography. It was of interest to find that six components were present. They had retention times identical with those of the six decafluorides now characterised. The large predominance of the 1H:2H-decafluorides was confirmed and shows clearly that migration of chlorine occurs only to a limited degree.

From qualitative observations, it appears that the relative rates of dehydrofluorinations of the decafluorides follow the pattern to be expected. The 1H:2H/-isomer forms an olefin very readily, whilst the 1H/2H-compound is the slowest to react, for reasons discussed earlier.[1] The 1H/4H- and 1H:3H/-isomers also react easily, the former slightly more readily. This is understandable, since the two axial hydrogen atoms are separated on each side by two $\rangle CF_2$ groups and so each should have slightly greater acidity than the hydrogens of the 1H:2H- and 1H:3H-series. Also, in the 1H/4H-compound the hydrogen atoms are far apart and on opposite sides of the *cyclo*hexane ring whilst in the 1H:3H/-compound they are close together. An interesting effect is the parallel between the proximity of hydrogen atoms in polyfluoro*cyclo*hexanes and their gas chromatography retention times and also their boiling points. Thus, in the decafluoride series, the two members with the hydrogens adjacent (1H:2H/- and 1H:3H/-) are retained longest and have the highest boiling points (91° and 89°, respectively). If the hydrogens are close together, intermolecular bindings appear to be stronger; the same effect is shown by nonafluoro*cyclo*hexanes.

EXPERIMENTAL

*Isolation of the decafluoro*cyclo*hexanes*

The mixture obtained from the fluorination of benzene,[1] after removal of compounds having boiling points <70°, was fractionally distilled using a heated vacuum-jacketed column (4 ft × ¾ in.) packed with Dixon gauze spirals ($\frac{1}{16} \times \frac{1}{16}$ in.). The fractionation was controlled by analytical gas chromatography (dinonyl phthalate/kieselguhr 1:2, temp. 80°, N_2 flow-rate 1·0 l/hr). Fractions were taken as follows:

Fraction A. This had b.p. 77–78°, and comprised 12–14 per cent of the mixture, giving a large flat region on the distillation curve. This fraction gave a single peak (no. 5 in Table 1[1]) on analytical gas chromatography, using dinonyl phthalate/kieselguhr packings even when large samples were injected (Found: C, 27·5; H, 1·0; F, 72·7. Calc. for $C_6H_2F_{10}$: C, 27·3; H, 0·8; F, 71·9%). However, with a column packing of silicone oil/silicone rubber[4] (1:10) (temp. 78°, N_2 flow-rate 1·0 l/hr.) the fraction was resolved into two components of approximately equal proportions; a column packing of tricresyl phosphate/kieselguhr (1:3) gave a less sharp resolution of the two components. The infra-red spectrum of the mixture was measured between 3000 and 650 cm^{-1} in the vapour state and displayed absorptions attributable to the 1H/4H- and 1H/3H-decafluoro*cyclo*hexanes prepared separately by cobaltic fluoride fluorination of two of the 1H:2H:4H-nonafluoro*cyclo*hexanes (see later). No other compounds were present.

An almost complete separation was effected, using preparative-scale gas chromatography in a tube 20 ft × 3·5 cm i.d. packed with tricresyl phosphate/kieselguhr 1:3 (temp 40°, N_2 flow-rate 9 l/hr). The two components were identified by infra-red spectroscopy as 1H/4H-decafluoro*cyclo*hexane containing about 9 per cent of the 1H/3H-isomer, and as the 1H/3H-compound, free of the other isomer.

Fraction B. This had b.p. 86·0–86·5°, and was 3–5 per cent of the mixture, giving a considerable flat part on the distillation curve. It gave a single peak (no. 6 in Table 1[1]) on analytical gas chromatography, even when large samples were injected and various packings used, viz. dinonyl phthalate/kieselguhr, tricresyl phosphate/kieselguhr, silicone oil/silicone rubber. It was 1H:4H/-*decafluoro*cyclo*hexane*, b.p. 86°, m.p. 40–41° (Found: C, 27·0; H, 0·8%).

Fractions with b.r. 70–77° and 78–86° were mixtures and no new components were detected by gas chromatography.

Fraction C. Material of b.r. 87–92° was shown by analytical gas chromatography to contain 4 compounds. These were the 1H:4H/-decafluoride (b.p. 86°) (peak 6[1]), 1H:4H/2H-nonafluoro*cyclo*hexane[3] (b.p. 92°) (peak 7[1]) and two new components (peaks 8 and 9[1]). Separation by distillation was impossible, so the fraction with the maximum concentration of the new compounds (Fraction C, b.r. 91·2–91·7°) was separated by preparative-scale gas chromatography (tube 16 ft × 3 cm packed with dinonyl phthalate/kieselguhr 1:2, temp. 100°, N_2 flow-rate 10 l./hr). The first and second compounds to be obtained in this way were the 1H:4H/-decafluoro*cyclo* hexane (b.p. 86°) and the 1H:4H/2H-nonafluoro*cyclo*hexane[3] (b.p. 92°). The third compound (b.p. 91°) was 1H:2H/-decafluoro*cyclo*hexane (peak 8). The gas chromatography retention times and infra-red absorption spectrum over the range 1800–700 cm^{-1}, were identical with those of the *cis*-isomer obtained by lithium aluminium hydride reduction of 1:2-dichlorodecafluoro*cyclo*hexane in ether.[1,2]

The fourth and last compound (peak 9) (b.p. 89°, m.p. 35–40°) (Found: C, 27·3; H, 0·8; F, 71·4%) was 1H:3H/-*decafluoro*cyclo*hexane*. The overall yield of the above two decafluorides was 0·5–1 per cent of the original polyfluoride mixture.

*Fluorination of nonafluoro*cyclo*hexanes*

Fluorination apparatus. This consisted of a horizontal copper tube (17 in. long; 2 in. i.d.; $\frac{1}{8}$ in. wall thickness) completely packed with a mixture of cobaltic fluoride (300 g) and $\frac{1}{2}$ in. nickel gauze cylinders (500 cc). The end plates were made from Yorkshire-type unions into which were brazed $\frac{1}{4}$ in. o.d. copper pipes. The tube was heated by three sectional heaters of the improved design described before.[1] The compounds, introduced at a steady rate as liquids from an electrically heated microburette, were vapourised, the vapours passed over the fluorinating agent, and the products were collected in a trap cooled by solid CO_2. When the addition was complete the apparatus was swept out for ca. 30 min with a slow stream of nitrogen, and the trap was then warmed to room temperature and the contents poured into water. After each fluorination the cobaltic fluoride in the reaction vessel was regenerated by passage at about 150° of fluorine (ca. 25 g) during 1$\frac{1}{2}$ hr. After being swept through with nitrogen, the reactor was again ready for use.

Fluorination of 1H/2H:4H-*nonafluoro*cyclo*hexane.* The nonafluoro*cyclo*hexane,[3] (16 g, b.p. 101°) was passed during 1 hr over cobaltic fluoride at about 150° in the vessel described above. Gas chromatographic analysis of the waxy solid product (17 g) (after the addition of a little ether to a small sample) revealed the presence of six components. The mixture (4·29 g) was separated by preparative-scale gas chromatography (column 16 ft × 3 cm, packed with dinonyl phthalate/kieselguhr 1:2, temp. 98°, N_2 flow-rate 9 l/hr) to give a trace of perfluoro*cyclo*hexane, b.p. 52°; undecafluoro*cyclo*hexane, b.p. 63° (0·32 g); 1H/2H-decafluoro*cyclo*hexane, b.p. 70° (0·18 g), 1H/4H-*decafluoro*cyclo*hexane*, b.p. 78°, (1·14 g) (Found: C, 27·2; H, 0·8%); 1H:3H/-decafluoro*cyclo*hexane, b.p. 89° (0·34 g); and unchanged 1H/2H:4H-nonafluoro*cyclo*hexane, b.p. 101° (1·23 g). These compounds had infra-red spectra identical with those of the analogous samples described above. The gas chromatography retention times were also the same.

Fluorination of 1H:4H/2H-*nonafluoro*cyclo*hexane*. The nonafluoro*cyclo*hexane (16 g, b.p. 93°) was passed during 40 min over cobaltic fluoride at about 150° to give a waxy solid product (15 g). A portion (4·4 g) of this was dissolved in ether and separated by preparative-scale gas chromatography (column 16 ft × 3 cm, dinonyl phthalate/kieselguhr 1 : 2, temp. 103°, N_2 flow-rate 9·0 l/hr) to give perfluoro*cyclo*hexane, b.p. 52° (0·01 g); undecafluoro*cyclo*hexane, b.p. 63° (0·54 g); 1H/2H-decafluoro*cyclo*hexane, b.p. 70° (0·09 g); 1H/3H-*decafluoro*cyclo*hexane*, b.p. 78° (0·55 g) (Found: C, 27·5; H, 1·0%); 1H:4H/-decafluoro*cyclo*hexane, b.p. 86° (0·50 g); and unchanged 1H:4H/2H-nonafluoro*cyclo*hexane, b.p. 93° (1·35 g). The compounds of this mixture were identified by their chromatographic retention times and by measurement of their infra-red absorption spectra, which were identical in all cases with those of analogous samples.

Dehydrofluorination of 1H:4H/-*decafluoro*cyclo*hexane*. The decafluoro*cyclo*hexane (1·5 g, b.p. 86°) was boiled for 4 hr with potassium hydroxide (1·5 g) in water (7·5 cc). The organic phase was separated, washed and dried ($MgSO_4$). Analytical vapour phase chromatographic examination of the product (dinonyl phthalate/kieselguhr 1 : 2, temp. 84°, N_2 flow-rate 1·2 l/hr) revealed three peaks at the same retention times as those from authentic specimens of [7,8] respectively, octafluoro*cyclo*hexa-1:4-, and -1:3-diene and 4H-nonafluoro*cyclo*hexene. No 3H-nonafluoro*cyclo*hexene[8] could be detected, even when large samples were injected.

In a preparative-scale reaction, the 1H:4H/-compound (10·00 g) was refluxed with potassium hydroxide (10 g) in water (50 cc) for 4½ hr. The organic layer (7·97 g) was separated, dried ($MgSO_4$) and fractionated in the preparative-scale gas chromatographic column[4] (16 ft × 3 cm packed with dinonyl phthalate/kieselguhr 1 : 2) to give octafluoro*cyclo*hexa-1:4-diene (1·34 g), octafluoro*cyclo*hexa-1:3-diene (0·50 g) and 4H-nonafluoro*cyclo*hexene (5·82 g). These had infra-red spectra in the vapour phase over the range 1800–700 cm^{-1} identical with those of specimens obtained previously.[7,8]

Oxidations of these olefins were carried out as described before,[5,7,8] and confirmed the earlier results. The 1:4-diene afforded difluoromalonic acid, the 1:3-diene gave tetrafluorosuccinic acid, and the 4H-olefin gave 3H-heptafluoroadipic acid. All were identified as their dianilinium and di-(*S*-benzylthiuronium) salts, which were obtained in good yields and with the correct elemental analyses.

Dehydrofluorination of 1H/4H-*decafluoro*cyclo*hexane*. The decafluoro*cyclo*hexane (4·5 g, b.p. 78°, obtained from the fluorination of 1H/2H : 4H-nonafluoro*cyclo*hexane) was kept at room temperature for 15 hr in contact with a solution of potassium hydroxide (1 g) in water (9 cc) with intermittent agitation. The organic layer was then separated and analysed by gas chromatography (dinonyl phthalate/kieselguhr 1 : 2, temp. 99°, N_2 flow-rate 1·15 l/hr); this revealed the presence of three products and the starting material, the retention times being identical with those of authentic samples of octafluoro*cyclo*hexa-1:4-diene, octafluoro*cyclo*hexa-1:3-diene, 4H-nonafluoro*cyclo*hexene and the unchanged decafluoro*cyclo*hexane. The mixture (3·05 g) was separated by preparative-scale gas chromatography (column 16 ft × 3 cm, dinonyl phthalate/kieselguhr 1 : 2, temp. 87°, N_2 flow-rate 10 l/hr) into octafluoro*cyclo*hexa-1:4-diene (0·12 g), octafluoro*cyclo*hexa-1:3-diene (0·01 g), 4H-nonafluoro*cyclo*hexene (2·03 g) and the *trans*-1H:4H-decafluoro*cyclo*hexane (0·30 g). No 3H-olefin was found. The 4H-nonafluoro*cyclo*hexene possessed an infra-red absorption spectrum over the range 1800–650 cm^{-1}, identical with that of authentic specimens.

When the 1H/4H-decafluoride (0·5 g) was refluxed for 2 hr with potassium hydroxide (0·5 g) in water (3·0 cc) the product contained only the 1:3- and 1:4-dienes, no starting material or 4H-olefin being present.

Dehydrofluorination of 1H/3H-*decafluoro*cyclo*hexane.* The decafluoro*cyclo*hexane (3·5 g, b.p. 78°, obtained by fluorination of the 1H:4H/2H-nonafluoro*cyclo*hexane), was refluxed with potassium hydroxide (0·8 g) in water (8 cc) for 8 hr. The organic layer was separated and analysed by gas chromatography (dinonyl phthalate/kieselguhr 1 : 2, temp. 92°, N_2 flow-rate 1·5 l/hr); this revealed the presence of four components (in addition to unchanged starting material) with retention times identical with those of authentic specimens of the octafluoro*cyclo*hexa-1:4- and -1:3-dienes and the 4H- and 3H-nonafluoro*cyclo*hexenes, respectively. The mixture (2·46 g) so obtained was separated by preparative scale gas chromatography (column 16 ft × 3 cm, dinonyl phthalate/kieselguhr 1 : 2, temp. 100°, N_2 flow-rate 8·9 l/hr) into octafluoro*cyclo*hexa-1:4-diene (ca. 0·01 g), octafluoro*cyclo*hexa-1:3-diene (ca. 0·01 g), 4H-nonafluoro*cyclo*hexene (1·09 g), 3H-nonafluoro*cyclo*hexene (0·99 g) and unchanged 1H/3H-decafluoro*cyclo*hexane (0·02 g); these fractions displayed infra-red absorption spectra identical with those of authentic specimens of these compounds over the range 1800–700 cm^{-1}.

Dehydrofluorination of 1H:3H/-*decafluoro*cyclo*hexane.* The decafluoro*cyclo*hexane (3·77 g, b.p. 89°) was refluxed for 3 hr with potassium hydroxide (4·0 g) in water (20 cc). The organic phase was separated, washed and dried ($MgSO_4$). Analytical gas chromatographic examination of the product (dinonyl phthalate/kieselguhr 1 : 2, temp. 86°, N_2 flow-rate 1·2 l/hr) revealed four peaks with the same retention times as those exhibited by authentic specimens of, respectively, octafluoro*cyclo*hexa-1:4- and -1:3-dienes, and 4H- and 3H-nonafluoro*cyclo*hexene. The mixed olefins (1·64 g) were separated in a preparative-scale gas chromatography column (16 ft × 3 cm, dinonyl phthalate/kieselguhr 1 : 2, temp. 88°, N_2 flow-rate 10 l/hr) to give octafluoro*cyclo*hexa-1:4-diene (0·41 g), octafluoro*cyclo*hexa-1:3-diene (0·26 g), 4H-nonafluoro*cyclo*hexene (0·41 g) and 3H-nonafluoro*cyclo*hexene (0·30 g). Each of the above components was identified by measurement of the infra-red absorption spectrum between 1800 and 700 cm^{-1} and comparison of them with those of authentic specimens.

Oxidation of 3H-*nonafluoro*cyclo*hex*-1-*ene.* The olefin (3·2 g), potassium permanganate (12·0 g), sodium bicarbonate (4·3 g) and water (70 cc) were shaken together for 18 hr at 65–70° in a rocking autoclave. After isolation as usual,[5] there was obtained a crude acidic product (2·3 g) which was distilled (130–140°/0·2 mm) to give a white hygroscopic solid (recovery 60 per cent). After being dried this 2H-*heptafluoroadipic acid* had m.p. 116–117° (Found: C, 26·9; H, 1·4%; equiv. 133. $C_6H_3O_4$ F_7 requires C, 26·5; H, 1·1%; equiv. 136). Reaction of the acid (0·2 g) with aniline in ether gave a solid which was recrystallised from chloroform–acetone to give a *dianilinium salt* (0·2 g), m.p. 169–170° (Found: C, 47·2; H, 3·7. $C_{18}H_{17}O_4N_2F_7$ requires C, 47·2; H, 3·7%). Treatment of the dianilium salt (0·038 g) with

S-benzylthiuronium chloride in water at pH 4 gave the *di-(S-benzylthiuronium) salt* (0·029 g), m.p. 232–233° (Found: C, 43·6; H, 3·7. $C_{22}H_{23}O_4N_4S_2F_7$ requires C, 43·7; H, 3·8%).

Preparation of a pure amide by esterification of the acid and treatment with ammonia was difficult because of elimination of fluoride ion during the ammonolysis.

With aqueous potassium hydroxide (1 N or 2 N) considerably more fluoride ion was lost from the 2H- than from 3H-heptafluoroadipic acid.

Comparative dehydrofluorinations of the 1H:4H- *and the* 1H:3H-*decafluoro*cyclo*hexanes.* The four compounds under test (0·5 g) were each covered with a solution of potassium hydroxide (0·8 g) in water (3 cc) and the mixtures kept at 50° for 1¼ hr with intermittent shaking (reaction conditions A). Test samples of the organic layers were then analysed qualitatively by gas chromatography (dinonyl phthalate/kieselguhr 1 : 2, temp. 96°, N_2 flow-rate 1·5 l/hr) under standard conditions. The reaction mixtures were then refluxed for a further 4 hr (reaction conditions B) and the organic layers were again subjected to gas chromatographic analysis under standard conditions. The results of the gas chromatographic analysis are given in Table 1.

Dipole moment measurements on 1H:4H-*decafluoro*cyclo*hexanes.* The apparatus and method employed were the same as before.[1] Measurements on the 1H:4H/-isomer (b.p. 86°), using solutions in benzene with concentrations up to 14 per cent by weight, gave an orientation polarisation of 139·4 ± 7·4 cc/mole, which is equivalent to a dipole moment of 2·59 ± 0·07 D. Only limited amounts of absolutely pure 1H/4H-isomer (b.p. 78°) were available, so that the solutions used had maximum concentrations of only ca. 4 per cent by weight. The measured orientation polarisation was 22·9 cc/mole, giving a dipole moment of 1·05 D, but the estimated limits of error in the former are ±22·2 cc/mole, so that the dipole moment could be in the range 0·2–1·5 D. However, it must be emphasised that the purpose of this experiment was to confirm the stereochemical structures of the two isomers. This has been done unequivocally, though the accuracy of the actual results obtained for the dipole moments, particularly for the 1H/4H-isomer, is not high.

Infra-red spectra. Some aspects of these are discussed in the following papers.[9,10] The complete spectra of the compounds described are included in the Documentation of Molecular Spectra issued by Butterworths.

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[10] J. Burdon and D. H. Whiffen *Tetrahedron* To be submitted shortly.