30. *Fluorocyclohexanes. Part V.** 1H : 4H/2H : 5H-, 1H : 5H/2H : 4H-, 1H : 2H/4H : 5H-, *and* 1H : 2H : 4H/5H-*Octafluoro*cyclo*hexane and Derived Compounds.*

By E. Nield, R. Stephens, and J. C. Tatlow.

Four octafluoro*cyclo*hexanes have been isolated from the products obtained by the fluorination of benzene with cobaltic fluoride. Of these, three give, on dehydrofluorination, the same four unsaturated compounds which have been separated by preparative-scale gas chromatography and identified by oxidation, spectroscopy, etc., as *1H* : *5H*- and *1H* : *4H*-hexafluoro*cyclo*hexa-1 : 4-diene, pentafluorobenzene, and *1H*,*4H*/*5H*-heptafluoro*cyclo*hexene. The fourth octafluoro*cyclo*hexane gives, on dehydrofluorination, the same 1 : 4-dienes, pentafluorobenzene, and *1H*,*4H* : *5H*/-heptafluoro*cyclo*hexene. A *1H* : *2H* : *4H* : *5H*-structure was thus indicated for all four octafluoro*cyclo*hexanes, and the stereochemistry of each was determined by further fluorination to give known nona- and deca-fluoro*cyclo*hexanes.

As described previously,[1-5] the mixture obtained on vapour-phase fluorination of benzene with cobalt trifluoride at about 150° yields a series of polyfluoro*cyclo*hexanes. The residue remaining after removal of the three major nonafluoro*cyclo*hexane fractions,[4, 5] *i.e.*, those having b. p. $>107°$, has now been examined, and four new octafluoro*cyclo*hexanes have been obtained from it. These fluorohydrocarbons (I, b. p. 118°, m. p. 62°; II, b. p. 125°, m. p. 94°; III, b. p. 133°, m. p. 88°; and IV, b. p. 136°, m. p. 30°) have been isolated by fractional distillation controlled by analytical gas chromatography.[6] Two of them (I and IV) were obtained pure directly from the distillation, but the other two required subsequent treatment for purification.

The compound of b. p. 125° (II) was obtained from a liquid fraction of boiling range 120—127°. This was a minor fraction and could not be separated further by distillation. However, it partly crystallised and the solid consisted largely of a mixture of an octafluoro*cyclo*hexane (II) and a small amount of perfluorodi*cyclo*hexyl. The former (II) was isolated pure by the zone-melting technique.[7] A pure specimen of perfluorodi*cyclo*hexyl was obtained from the crude solid mixture by treatment with aqueous potassium hydroxide. Dehydrofluorination of the fluorohydrocarbon (II) (see below) gave liquid unsaturated products from which perfluorodi*cyclo*hexyl crystallised in the cold. This fluorocarbon may arise from the fluorination of diphenyl, formed by the combination of phenyl radicals which could result from an initial removal of hydrogen from benzene by the fluorinating agent. Such intermediate species obviously react mainly to give fluorobenzenes and thence fluoro*cyclo*hexanes. Alternatively, the perfluorodi*cyclo*hexyl could be formed by the combination of partially fluorinated *cyclo*hexyl, *cyclo*hexenyl, or *cyclo*hexadienyl intermediates arising during the fluorination. Dimerisations of this general type occur frequently during reaction with elementary fluorine, particularly in the liquid phase.[8,9] Though they are not usually encountered in processes involving cobaltic fluoride, a similar effect has been noted [10] in the fluorination of benzene with manganic fluoride.

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* Part IV, preceding paper, *q.v.* for nomenclature.

[1] Smith and Tatlow, *J.*, 1957, 2505.

[2] Stephens and Tatlow, *Chem. and Ind.*, 1957, 821.

[3] Evans, Godsell, Stephens, Tatlow, and Wiseman, *Tetrahedron*, 1958, **2**, 183.

[4] Godsell, Stacey, and Tatlow, *Tetrahedron*, 1958, **2**, 193.

[5] Stephens, Tatlow, and Wiseman, preceding paper.

[6] Evans and Tatlow, *J.*, 1955, 1184.

[7] Herington, Handley, and Cook, *Chem. and Ind.*, 1956, 292; Parr, *Roy. Inst. Chem., Lectures, Monographs, and Reports*, 1957, No. 3.

[8] Miller, Ehrenfeld, Phelan, Prober, and Reed, *Ind. Eng. Chem.*, 1947, **39**, 401.

[9] Smith, Stacey, Tatlow, Dawson, and Thomas, *J. Appl. Chem.*, 1952, **2**, 97.

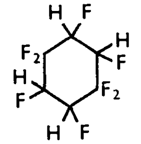
[10] Fear and Thrower, *ibid.*, 1955, **5**, 353.

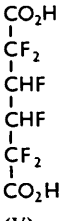
The mother-liquor remaining from the initial crystallisation of the fraction of boiling range 120—127° was shown by analytical gas chromatography to contain six components, and was separated by preparative-scale gas chromatography[11] into five fractions. Four of the compounds present have been characterised. The first component was identified by infrared spectroscopy as perfluorodi*cyclo*hexyl. The second was identical with a hexafluoro*cyclo*hexene to be described in a later paper[12] and was oxidised[13] by potassium permanganate in acetone to give the known[4] (±)-3*H* : 4*H*-hexafluoroadipic acid (V), showing it to be 1*H* : 2*H*,4*H*/5*H*-hexafluoro*cyclo*hexene (VI). The third sub-fraction was a mixture of two saturated hydrofluorocarbons but their identification has been delayed so far by the very small amounts available. The fourth component was identified (see Part IV[5]) as 1*H* : 2*H* : 4*H*/-nonafluoro*cyclo*hexane, b. p. 124°. The fifth sub-fraction was shown by infrared spectroscopy to be 1*H* : 5*H*/2*H* : 4*H*-octafluoro*cyclo*hexane (II).

The fraction of the polyfluoro*cyclo*hexane mixture having b. p. 133° (III) was obtained as a liquid from the distillation but rapidly crystallised, the crystals being freed from liquid impurities by washing with ether. This gave specimens showing no minor peaks in gas chromatography and giving correct analyses for an octafluoro*cyclo*hexane.

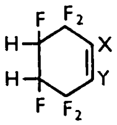
The four octafluoro*cyclo*hexanes (I—IV) were dehydrofluorinated with aqueous potassium hydroxide to give, in each case, a mixture of four compounds, as indicated by gas chromatography. The gas-chromatographic retention times also suggested that the octafluoro*cyclo*hexanes with b. p.s 118° (I), 125° (II), and 136° (IV) each gave the same four products, but that the compound with b. p. 133° (III) gave three products which were the same as those from the isomers (I, II, and IV), the fourth, that of longest retention time, being different. The compounds were isolated by preparative-scale gas chromatography, and infrared spectroscopy confirmed the above conclusions.

(I) 1*H*a : 4*H*e/2*H*a : 5*H*e
(II) 1*H*a : 5*H*a/2*H*a : 4*H*a
(III) 1*H*a : 2*H*e/4*H*a : 5*H*e
(IV) 1*H*e : 2*H*a : 4*H*a/5*H*a



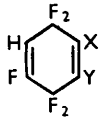

$\mathrm{CO_2H{-}CF_2{-}CHF{-}CHF{-}CF_2{-}CO_2H}$

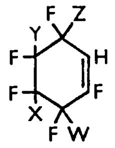
(V)



(VI) X=Y=H; 4*H*/5*H*
(VII) X=H, Y=F; 4*H*/5*H*
(VIII) X=H, Y=F; 4*H*:5*H*/

(IX) X=H, Y=F
(X) X=F, Y=H





	W	X	Y	Z
(XI)	H	F	F	F
(XII)	F	F	F	H
(XIII)	F	F	H	F
(XIV)	F	H	F	F

The unsaturated product with the shortest chromatographic retention time had b. p. 71°, and analysed as a hexafluoro*cyclo*hexadiene. On oxidation with potassium permanganate in acetone it gave difluoromalonic acid. There was no strong selective absorption in the range 2400—3000 Å. Two -C=C- absorption bands[14] of roughly similar strengths in the infrared spectrum at 1744 and 1711 cm.$^{-1}$ and a $\geqslant$C–H band[15] at 3082 cm.$^{-1}$ indicated a 1 : 4-diene system with two -CH=CF- groups, and an unsymmetrical arrangement; *i.e.*, the compound was 1*H* : 5*H*-hexafluoro*cyclo*hexa-1 : 4-diene (IX).

This structure was substantiated by fluorination of the diene (IX) with cobaltic fluoride in a small static cylindrical reaction vessel.[3] The liquid product was shown by gas

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[11] Evans, Massingham, Stacey, and Tatlow, *Nature*, 1958, **182**, 591.
[12] Nield, Stephens, and Tatlow, unpublished work.
[13] Burdon and Tatlow, *J. Appl. Chem.*, 1958, **8**, 293.
[14] Burdon and Whiffen, *Spectrochim. Acta*, 1958, **12**, 139.
[15] Steele and Whiffen, *Tetrahedron*, 1958, **3**, 181.

chromatography to contain eight components, 1*H*/3*H*- and 1*H* : 3*H*/-decafluoro*cyclo*hexanes being isolated and identified. These two must have arisen by saturation of the double bonds of the diene and established the 1 : 3-disposition of the hydrogen atoms since no isomeric decafluorides were present. A complicating feature of this fluorination, however, was the isolation of 1*H* : 3*H*-octafluoro*cyclo*hexene (XI). The absence of other decafluoro-compounds from the mixture suggested that the 1*H* : 3*H*- arrangement must be preserved in compound (XI). Dehydrofluorination of it afforded the known [4, 5] 1*H*- and 2*H*-heptafluoro*cyclo*hexa-1 : 3-dienes, presumably by 1 : 2- and 1 : 4-elimination respectively. Oxidation with potassium permanganate in the presence of sodium hydrogen carbonate gave the known [6, 3] 2*H*-heptafluoroadipic acid. There was an infrared absorption band at 1715 cm.$^{-1}$, typical of the group –CH=CF– and $\geqslant$C–H bands at 3100 and 2961 cm.$^{-1}$ characteristic of hydrogen carried respectively on and α to a double bond. The 1*H* : 3*H*- arrangement (XI) is proved by the formation of two conjugated dienes upon dehydrofluorination. The isomeric 1*H* : 6*H*-octafluoro*cyclo*hexene (XII) should give only 2*H*-heptafluoro*cyclo*hexa-1 : 3-diene. This compound (XII) has been prepared [16] in other work; it differs from compound (XI) and in fact does give only the 2*H*-1 : 3-diene with alkali. Compound (XI) must have arisen by selective fluorination of a double bond in a 1*H* : 3*H*-hexafluoro*cyclo*hexa-1 : 3-diene formed by a rearrangement of the diene (IX). Other cases of the migration of double bonds in cyclic 1 : 4- and 1 : 3-dienes are now known [17] and examples of the same type were observed in similar fluorinations described [5] in Part IV. The other five components of the original mixture obtained from the fluorination were those expected from a 1*H* : 5*H*-hexafluoro*cyclo*hexa-1 : 4-diene (IX), *viz.*, perfluoro*cyclo*hexane, undecafluoro*cyclo*hexane, 1*H*-nonafluoro*cyclo*hexene, unchanged diene, and 1*H* : 5*H*-heptafluoro*cyclo*hexene (XIII) which were all identified by infrared spectroscopy.

The second compound from the original dehydrofluorinations of the octafluoro*cyclo*hexanes (I—IV) had b. p. 75° and was shown to be the isomeric 1*H* : 4*H*-hexafluoro*cyclo*hexa-1 : 4-diene (X) by the same methods. Thus, oxidation with potassium permanganate in acetone gave difluoromalonic acid and fluorination with cobalt trifluoride gave a mixture containing six components, identified by infrared spectroscopy and gas chromatography as perfluoro*cyclo*hexane, undecafluoro*cyclo*hexane, 1*H*-nonafluoro*cyclo*hexene, 1*H*/4*H*- and 1*H* : 4*H*/-decafluoro*cyclo*hexane, and 1*H* : 4*H*-octafluoro*cyclo*hexene (XIV). This fluorination was not complicated by migration of the type previously observed since such a change would not produce any additional products. The diene (X) did not show selective absorption in its ultraviolet spectrum over the range 2400—3000 Å. In the infrared spectrum it had a $\geqslant$C–H band at 3087 cm.$^{-1}$ and –C=C– bands at 1707 (very strong) and 1737 cm.$^{-1}$ (weak). Two bands would not be expected for a symmetrical molecule of this type and the effect is considered to arise from the non-planarity of the *cyclo*hexa-1 : 4-diene ring,[14] this being supported by the very unequal intensities of the two bands. Models indicate that a boat form of this diene ring is less strained than a planar one.

The third dehydrofluorination product of the octafluoro*cyclo*hexanes (I—IV) had b. p. 85° and was characterised as pentafluorobenzene in the manner already described.[2] Further reactions of this important aromatic compound are reported in the following paper.

The fourth unsaturated product was obtained from the dehydrofluorinations of three octafluoro*cyclo*hexanes (I, II, and IV) and had b. p. 104°. Its analysis indicated a heptafluoro*cyclo*hexene and it was found to be identical with the 1*H*,4*H*/5*H*-heptafluoro*cyclo*hexene (VII) described earlier.[4] A different heptafluoro*cyclo*hexene (VIII) was obtained from the dehydrofluorination of the octafluoro*cyclo*hexane (III) of b. p. 133°. On oxidation with potassium permanganate in acetone compound (VIII) gave the known [5] *meso*-3*H* : 4*H*-hexafluoroadipic acid (V). There was an infrared absorption band at 1720 cm.$^{-1}$, characteristic of a –CH=CF– group, and a $\geqslant$C–H band at 2980 cm.$^{-1}$ indicating the presence

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[16] Evans and Tatlow, unpublished work.

[17] Gething, Patrick, and Tatlow, unpublished work.

of hydrogen on the carbon atoms β to this double bond. Compound (VIII) was thus 1*H*,4*H* : 5*H*/-heptafluoro*cyclo*hexene.

A 1*H* : 2*H* : 4*H* : 5*H*-system was thus indicated for the four octafluoro*cyclo*hexanes described. By eliminations of the normal type, a 1*H* : 2*H* : 3*H* : 4*H*-system on dehydrofluorination could possibly give four stable hexafluoro*cyclo*hexa-1 : 3-dienes but no stable hexafluoro*cyclo*hexa-1 : 4-diene, and a 1*H* : 2*H* : 3*H* : 5*H*-system would give no stable octafluoro*cyclo*hexa-1 : 3- or -1 : 4-diene. The term " stable dienes " here means compounds without >CHF groups. 1 : 3- or 1 : 4-Dienes with >CHF groups are in effect aromatic fluoro-compounds with hydrogen fluoride added to the ring and it is unlikely that they would survive in the relatively drastic dehydrofluorination conditions employed. No intermediates of this type have been found so far in any of the reactions which have given aromatic fluoro-compounds.

The stereochemical structures of the octafluoro*cyclo*hexanes (I—IV) were deduced by further fluorination to the known nona- and deca-fluoro*cyclo*hexanes described earlier.[1–5] The isomer (I) of b. p. 118° gave 1*H*a : 4*H*e/2*H*a-nonafluoro*cyclo*hexane and 1*H*a/2*H*a-, 1*H*a/3*H*e-, and 1*H*a : 4*H*e/-decafluoro*cyclo*hexane, together with undecafluoro*cyclo*hexane and perfluoro*cyclo*hexane. This establishes the stereochemical structure as 1*H*a : 4*H*e/2*H*a : 5*H*e-octafluoro*cyclo*hexane (I). In the same way, the isomer (II) of b. p. 125° gave 1*H*a/2*H*a : 4*H*a-nonafluoro*cyclo*hexane, 1*H*a/2*H*a-, 1*H*a/4*H*a-, and 1*H*a : 3*H*a/-decafluoro*cyclo*hexane, undecafluoro*cyclo*hexane, and perfluoro*cyclo*hexane. These compounds can arise only from a 1*H*a : 5*H*a/2*H*a : 4*H*a-octafluoro*cyclo*hexane (II). Likewise the isomer of b. p. 133° was shown to be the 1*H*a : 2*H*e/4*H*a : 5*H*e-compound (III) since it gave on further fluorination 1*H*a : 2*H*e/4*H*a-nonafluoro*cyclo*hexane, and 1*H*a/4*H*a-, 1*H*a/3*H*e-, and 1*H*a : 2*H*e/-decafluoro*cyclo*hexane, together with the derived undecafluoro- and perfluoro-*cyclo*hexanes. The fourth octafluoro*cyclo*hexane (IV) of b. p. 136°, on fluorination, gave a mixture of all four 1*H* : 2*H* : 4*H*-nonafluoro*cyclo*hexanes and five of the derived decafluoro*cyclo*hexanes, besides undecafluoro- and perfluoro-*cyclo*hexanes. Hence the parent compound is the 1*H*e : 2*H*a : 4*H*a/5*H*a-octafluoro*cyclo*hexane (IV). The fifth octafluoro-*cyclo*hexane, the 1*H*a : 2*H*e : 4*H*e : 5*H*a/-isomer, which contains the structural features of the three highest-boiling decafluoro*cyclo*hexanes (which are in fact *cis*), is as yet unknown. It is expected to boil at about 150° or above, and should give only the 1*H*e : 2*H*a : 4*H*a/-nonafluoro*cyclo*hexane on further fluorination. Since this nonafluoro-compound is present in the polyfluoro*cyclo*hexane mixture in only small amounts the fifth octafluoro-compound also may well be a minor constituent.

The structural allocations arrived at in this way are in general agreement with the results of the dehydrofluorinations. The octafluoro*cyclo*hexanes of b. p. 133° and 136° lost hydrogen fluoride more readily than did the two isomers of b. p. 118° and 125°. The isomer of b. p. 133° gave a higher proportion of the hexafluoro*cyclo*hexa-1 : 4-dienes and less pentafluorobenzene, as would be expected from its 1*H*a : 2*H*e/4*H*a : 5*H*e-system which should undergo *trans*-eliminations [1,5] in the –CHF–CHF– groupings with comparative ease. Likewise, the 1*H* : 2*H* : 4*H*/5*H*-isomer was dehydrofluorinated at room temperature to give almost exclusively the 1*H*,4*H*/5*H*-heptafluoro*cyclo*hexene (VII) by an internal *trans*-elimination in the *cis*-CHF–CHF-system. Further dehydrofluorination of this olefin was, however, much more difficult. Further proof that the 4*H*/5*H*-arrangement in this *cyclo*hexene (VII) is *trans* was provided [4] by oxidation to the hexafluoroadipic acid (V), which gives a resolvable brucine salt. On the other hand, the existence of two *cis*-arrangements in the 1*H*a : 2*H*e/4*H*a : 5*H*e-isomer, b. p. 133° (III), was supported by oxidation of the derived 1*H*,4*H* : 5*H*/-heptafluoro*cyclo*hexene (VIII) to the unresolvable [5] *meso*-3*H* : 4*H*-hexafluoroadipic acid (V).

The relatively rapid formation of pentafluorobenzene on dehydrofluorination of the 1*H* : 4*H*/2*H* : 5*H*-isomer (I) and the comparative difficulty of dehydrofluorinating the 1*H*,4*H*/5*H*-heptafluoro*cyclo*hexene (VII) indicate that some simultaneous elimination of hydrogen fluoride occurs, and that this *cyclo*hexene is not an intermediate for all of the aromatic compound formed.

EXPERIMENTAL

Techniques.—Oxidations, gas chromatography, and infrared measurements were carried out as before,[5] unless otherwise stated.

1H : 4H/2H : 5H-, 1H : 5H/2H : 4H-, 1H : 2H/4H : 5H-, and 1H : 2H : 4H/5H-*Octafluoro*cyclo*hexane*.—Fractional distillation controlled by analytical gas chromatography of the partly fluorinated *cyclo*hexane mixture [5] having b. p. >107° gave the following fractions:

Fraction (*A*). This was 1H : 4H/2H : 5H-*octafluoro*cyclo*hexane*, m. p. 60—62°, b. p. 117—118°. It gave a single peak (No. 11 in the table of results given earlier [1]) in analytical gas chromatography (Found: C, 31·3; H, 1·8. $C_6H_4F_8$ requires C, 31·6; H, 1·8%). The yield was approximately 5—10% of the original mixture with a cobaltic fluoride reaction vessel at about 150°; this yield may be increased by using a lower temperature.

Fraction (*B*). This had boiling range 120—127° (*ca.* 0·5% of the original mixture) and was initially a liquid at 15°, but on being kept deposited a highly crystalline solid (i) which was removed by filtration from the mother-liquor (ii). The solid (i) had m. p. 86—88° but was impure. Application of the zone-melting technique [7] [tube, 9″ × 0·25″ (internal diameter); 20 passes of heated zone at tube movement of 3″/hr.] afforded, as a top zone, 1H : 5H/2H : 4H-*octafluoro*cyclo*hexane*, m. p. 93—94°, b. p. 125° (Found: C, 31·8; H, 2·1%). The yield was about 0·2% of the original polyfluoride mixture.

The main impurity in the original deposit (i) was perfluorodi*cyclo*hexyl which was isolated after dehydrofluorination of the crude octafluoride (see below).

The mother-liquor (ii) (7·8 g.) was separated into its constituents by preparative-scale gas chromatography (column A) to give: (*a*) a small amount of perfluorodi*cyclo*hexyl; (*b*) 1*H* : 2*H*, 4*H*/5*H*-hexafluoro*cyclo*hexene (1·4 g.); (*c*) a mixed fraction (0·3 g.); (*d*) 1*H* : 2*H* : 4*H*/-nonafluoro*cyclo*hexane (2·7 g.), b. p. 124°; (*e*) 1*H* : 5*H*/2*H* : 4*H*-octafluoro*cyclo*hexane (1·4 g.), b. p. 125°. Perfluorodi*cyclo*hexyl was identified by its infrared spectrum which was identical with that of an authentic specimen.[18] Sub-fraction (*b*) was characterised by oxidation and by the identity of its infrared spectrum with that of material obtained from another source.[12] Sub-fraction (*c*) was a mixture of two saturated compounds but the very small amount available has prevented identification. Sub-fraction (*d*) was identified as described in Part IV.[5] Sub-fraction (*e*) was identified as the octafluoro*cyclo*hexane of b. p. 125°, by infrared spectroscopy.

Fraction (*C*). This had b. p. 133° but rapidly crystallised, and was then washed with a small amount of diethyl ether. It was 1H : 2H/4H : 5H-*octafluoro*cyclo*hexane*, m. p. 86—88° (Found: C, 31·2; H, 1·6%). The yield was approximately 0·2% of the partially fluorinated mixture.

Fraction (*D*). This was 1H : 2H : 4H/5H-*octafluoro*cyclo*hexane*, b. p. 136°, m. p. 30° (Found: C, 31·5; H, 1·7%), and constituted approx. 5—10% of the partially fluorinated *cyclo*hexane mixture.

The intermediate fractions having boiling ranges 107—117°, 118—120°, 127—133°, and 133—136° contained no other compounds.

Dehydrofluorination of 1H : 4H/2H : 5H-*Octafluoro*cyclo*hexane*.—The octafluoro*cyclo*hexane (34·0 g.; b. p. 118°), potassium hydroxide (60·0 g.), and water (60 c.c.) were heated together under reflux for 4½ hr. with stirring. The organic phase (21·3 g.) was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography (105°; N_2 flow-rate 1·0 l./hr.) revealed four peaks. A typical separation of the mixture (4·0 g.) in the preparative-scale gas chromatography column A gave: (i) a mixture (0·4 g.) of 1*H* : 5*H*- and 1*H* : 4*H*-hexafluoro*cyclo*hexa-1 : 4-dienes; (ii) *pentafluorobenzene* (2·6 g.), b. p. 85°, n_D^{18} 1·3931 (Found: C, 42·8; H, 0·7; F, 57·1. C_6HF_5 requires C, 42·9; H, 0·7; F, 56·5%); and (iii) 1*H*,4*H*/5*H*-heptafluoro*cyclo*-hexene (0·7 g.), b. p. 104°, n_D^{19} 1·3420 (Found: C, 34·9; H, 1·3. Calc. for $C_6H_3F_7$: C, 34·6; H, 1·45%), which had an infrared spectrum identical with that of the compound described by Godsell, Stacey, and Tatlow.[4]

The mixture of hexafluoro*cyclo*hexa-1 : 4-dienes (2·03 g.) was separated by further preparative-scale gas chromatography (76°; N_2 flow-rate 9·0 l./hr.) into 1H : 5H-*hexafluoro*cyclo*hexa*-1 : 4-*diene* (1·08 g.), b. p. 71°, n_D^{20} 1·3391 (Found: C, 38·1; H, 1·2; F, 60·3. $C_6H_2F_6$ requires C, 38·3; H, 1·1; F, 60·6%), and 1H : 4H-*hexafluoro*cyclo*hexa*-1 : 4-*diene* (0·33 g.), b. p. 75°, n_D^{17} 1·3419 (Found: C, 38·2; H, 1·2%).

Characterisation of 1H : 5H-*Hexafluoro*cyclo*hexa*-1 : 4-*diene*.—(a) *Oxidation.* The diene

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[18] Barbour, Barlow, and Tatlow, *J. Appl. Chem.*, 1952, **2**, 127.

(0·96 g.; b. p. 71°), potassium permanganate (1·8 g.), and dry acetone (300 c.c.) gave difluoromalonic acid (60%).

(b) *Fluorination.* The diene (6·0 g.), diluted with nitrogen (4—6 l./hr.), was passed during ½ hr. over cobaltic fluoride at 75—80° in the vessel described before.[3] Gas chromatography of the liquid product (4·1 g.) revealed eight components, which were separated by preparative-scale gas chromatography (column A; 86°; N_2 flow-rate 10 l./hr.), which gave a trace of perfluoro*cyclo*hexane, followed by undecafluoro*cyclo*hexane, 1*H*-nonafluoro*cyclo*hexene, and starting material, 1*H*/3*H*-decafluoro*cyclo*hexane (1·5 g.), 1*H* : 5*H*-octafluoro*cyclo*hexene (0·1 g.), 1H : 3H-*octafluoro*cyclo*hexene* (0·26 g.), n_D^{19} 1·3223 (Found: C, 31·6; H, 0·8. $C_6H_2F_8$ requires C, 31·9; H, 0·9%), and 1*H* : 3*H*/-decafluoro*cyclo*hexane (0·24 g.). All but the 1*H* : 3*H-cyclo*hexene were identified by their infrared spectra and their gas-chromatographic retention times.

(c) *Spectroscopy.* The diene showed two infrared bands of appreciable strength, at 1744 and 1711 cm.$^{-1}$, suggesting [14] two –CH=CF– groups in a 1 : 4-system. A $\geqslant$C–H band at 3082 cm.$^{-1}$ is typical [15] of olefinic hydrogen. There was no selective absorption in the range 2400—3000 Å.

Characterisation of 1H : 3H-*Octafluoro*cyclo*hexene.*—(a) *Dehydrofluorination.* The octafluoro*cyclo*hexene (0·2 g.), potassium hydroxide (4·0 g.), and water (2 c.c.) were shaken together at 15° for 1 hr. The organic phase was distilled out *in vacuo*, then redistilled *in vacuo* from phosphoric oxide, and the product (0·1 g.) was shown by gas chromatography to contain two components in addition to a very small amount of the unchanged *cyclo*hexene. The infrared absorption spectrum of the mixture established that the compounds were 1*H*- and 2*H*-heptafluoro*cyclo*hexa-1 : 3-diene.[4, 5] The relative peak strengths of the two isomers indicated the presence of about three times as much of the 1*H*- as of the 2*H*-isomer. The gas-chromatographic retention times and peak areas were in agreement with these results.

(b) *Oxidation.* The octafluoro*cyclo*hexene (0·4 g.), potassium permanganate (0·7 g.), sodium hydrogen carbonate (1·5 g.), and water (50 c.c.) were shaken together at 15° for 40 hr. The solution was then decolorised by sulphur dioxide, acidified by concentrated sulphuric acid (5 c.c.), and extracted continuously with ether. The ethereal extract was dried ($MgSO_4$), filtered, and evaporated, to leave the crude 2*H*-heptafluoroadipic acid (0·3 g.). The dianilinium salt was prepared in the usual way [6, 3] and had m. p. 170° (from acetone–chloroform) (Found: C, 47·2; H, 3·8. Calc. for $C_{18}H_{17}O_4N_2F_7$: C, 47·2; H, 3·7%). From the anilinium salt, di-(*S*-benzylthiuronium) 2*H*-heptafluoroadipate was prepared. After recrystallisation from water it had m. p. 228° (depressed on admixture with the 3*H*-isomer) (Found: C, 43·5; H, 3·8. Calc. for $C_{22}H_{23}O_4N_4S_2F_7$: C, 43·7; H, 3·8%) (lit.,[3] m. p. 169—170° and 232—233°, respectively).

(c) *Spectroscopy.* The *cyclo*hexene showed an infrared absorption band at 1715 cm.$^{-1}$, typical of the grouping –CH=CF–, and $\geqslant$C–H bands at 3100 and 2961 cm.$^{-1}$ characteristic of hydrogen located respectively on a double bond and on an α-carbon atom.

Characterisation of 1H : 4H-*Hexafluoro*cyclo*hexa*-1 : 4-*diene.*—(a) *Oxidation.* The diene (1·0 g.), potassium permanganate (3·2 g.), and dry acetone (300 c.c.) gave difluoromalonic acid (55%).

(b) *Fluorination.* The diene (4·1 g.) diluted with nitrogen (4—6 l./hr.) was passed during 20 min. over cobaltic fluoride at 65—70° in the way described previously. Gas chromatography of the liquid product (2·3 g.) revealed five components which were separated by preparative-scale gas chromatography (column A; 110°; N_2 flow-rate 8·8 l./hr.) into perfluoro*cyclo*hexane (trace), undecafluoro*cyclo*hexane (trace), 1*H*-nonafluoro*cyclo*hexene (trace), 1*H*/4*H*-decafluoro*cyclo*hexane (0·8 g.), and a mixture (0·6 g.) of 1*H* : 4*H*/-decafluoro*cyclo*hexane and 1*H* : 4*H*/-octafluoro*cyclo*hexene. These compounds were identified by their infrared spectra and by identity of gas-chromatographic retention times.

(c) *Spectroscopy.* The diene showed two bands, typical of two –CH=CF– groups arranged 1 : 4, at 1707 and 1737 cm.$^{-1}$, the latter being appreciably the weaker. There was a $\geqslant$C–H band at 3087 typical of olefinic hydrogen. No selective absorption was shown over the range 2400—3000 Å.

Dehydrofluorination of 1H : 5H/2H : 4H-*Octafluoro*cyclo*hexane.*—The crude octafluoro*cyclo*hexane [50·0 g.; m. p. 86—88°; fraction B (i) above], potassium hydroxide (100 g.), and water (100 c.c.) were heated together under reflux for 18 hr. The organic phase (30·0 g.) was separated whilst still warm and was washed with water. When cooled it deposited crystals (5·4 g.) which were filtered off. These were perfluorodi*cyclo*hexyl, and after recrystallisation from light petroleum (b. p. 80—100°) had m. p. 77—78° (Found: C, 25·1; F, 74·9. Calc. for $C_{12}F_{22}$: C, 25·6;

F, 74·4%). The infrared absorption spectrum was identical with that of an authentic specimen, prepared [18] by fluorination of diphenyl at 350°.

The liquid product was dried ($MgSO_4$) and shown by gas chromatography to contain four components with retention times identical with those of the four products isolated from the octafluoro*cyclo*hexane of b. p. 118°. Separation (4·5 g.) gave a mixture of 1*H* : 5*H*- and 1*H* : 4*H*-hexafluoro*cyclo*hexa-1 : 4-diene (0·45 g.), pentafluorobenzene (1·8 g.), and 1*H*,4*H*/5*H*-heptafluoro*cyclo*hexene (1·2 g.), all having correct infrared spectra.

The pure octafluoro*cyclo*hexane (8·0 g.; b. p. 125°; m. p. 93—94°), potassium hydroxide (16 g.), and water (16 c.c.) were stirred mechanically and refluxed for 2 hr. Isolation and identification as before afforded only mixed dienes (0·3 g.), pentafluorobenzene (2·1 g.), and 1*H*,4*H*/5*H*-heptafluoro*cyclo*hexene (0·9 g.).

Dehydrofluorination of 1H : 2H/4H : 5H-*Octafluoro*cyclo*hexane*.—The octafluoro*cyclo*hexane (8·0 g.; b. p. 133°), potassium hydroxide (16·0 g.), and water (16 c.c.) were shaken vigorously at 15° for 24 hr. The organic phase (4·9 g.) was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography revealed four components. Separation by preparative-scale gas chromatography (column A; 110°; N_2 flow-rate 7·0 l./hr.) gave: (i) 1*H* : 5*H*-hexafluoro*cyclo*hexa-1 : 4-diene (1·7 g.); (ii) 1*H* : 4*H*-hexafluoro*cyclo*hexa-1 : 4-diene (0·8 g.); (iii) pentafluorobenzene (0·3 g.); and (iv) 1H,4H : 5H/-*heptafluoro*cyclo*hexene* (1·35 g.), n_D^{23} 1·3430 (Found: C, 34·7; H, 1·5%). The first three fractions were identified by comparison of chromatographic retention times and infrared spectra with those of authentic specimens.

Characterisation of 1H,4H : 5H/-*Heptafluoro*cyclo*hexene*.—(a) *Oxidation*. The monoene (0·3 g.) was oxidised with potassium permanganate (0·8 g.) in dry acetone (100 c.c.) as described previously. Isolation as usual gave dianilinium *meso*-3*H* : 4*H*-hexafluoroadipate (0·6 g.) which after recrystallisation from acetone–chloroform had m. p. 201—202° (Found: C, 49·0; H, 4·0. Calc. for $C_{18}H_{18}O_4N_2F_6$: C, 49·1; H, 4·1%). This (0·20 g.) gave di-(*S*-benzylthiuronium) *meso*-3*H* : 4*H*-hexafluoroadipate (0·25 g.), m. p. 228—229° undepressed on admixture with a sample [5] of the salt of the *meso*-acid but depressed on admixture with one [4] of the racemic acid (Found: C, 45·0; H, 4·0. Calc. for $C_{22}H_{24}O_4N_4S_2F_6$: C, 45·0; H, 4·1%) (lit.,[5] m. p. 200—201° and 228—229°, respectively).

(b) *Spectroscopy*. The *cyclo*hexene showed an infrared absorption band at 1720 cm.$^{-1}$, typical of the group –CH=CF–, and >C–H bands at 2982 and 3087 cm.$^{-1}$ typical of hydrogen placed respectively β to the double bond and on it.

Dehydrofluorination of 1H : 2H : 4H/5H-*Octafluoro*cyclo*hexane*.—The octafluoro*cyclo*hexane (30·0 g.; b. p. 136°), potassium hydroxide (60 g.), and water (60 c.c.) were shaken together at room temperature for 7 hr. The organic phase (23·7 g.) was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography revealed the same four compounds as were obtained from the isomers of b. p. 118° and 125°, but the two dienes and pentafluorobenzene were present in traces only. By preparative-scale gas chromatography (column B), 1*H*,4*H*/5*H*-heptafluoro*cyclo*hexene (18·0 g.), b. p. 104°, n_D^{29} 1·3420, was isolated.

The octafluoro*cyclo*hexane (10·0 g.; b. p. 136°), potassium hydroxide (40 g.), and water (40 c.c.) were kept at 100° for 2 hr. with continuous stirring. The organic phase (4·1 g.) was shown to contain 1*H* : 5*H*- and 1*H* : 4*H*-hexafluoro*cyclo*hexa-1 : 4-diene (11% and 3%, respectively), pentafluorobenzene (44%), and 1*H*,4*H*/5*H*-heptafluoro*cyclo*hexene (42%).

Fluorination of 1H : 4H/2H : 5H-*Octafluoro*cyclo*hexane*.—The octafluoro*cyclo*hexane (7·5 g.; b. p. 118°) was passed during 25 min. over cobaltic fluoride at about 150° in the vessel described before.[3] Gas chromatography of the waxy product (7·8 g.) (after the addition of sufficient ether to a small portion to give a liquid sample) revealed seven components with retention times identical with those of perfluoro*cyclo*hexane, undecafluoro*cyclo*hexane, 1*H*/2*H*-decafluoro*cyclo*hexane, 1*H*/3*H*-decafluoro*cyclo*hexane, 1*H* : 4*H*/-decafluoro*cyclo*hexane, 1*H* : 4*H*/2*H*-nonafluoro*cyclo*hexane, and unchanged 1*H* : 4*H*/2*H* : 5*H*-octafluoro*cyclo*hexane, as established by enrichment of the fluorination mixture with authentic samples [3,4] of these compounds. The nonafluoro-compound and unchanged octafluoride were separated from the mixture by preparative-scale gas chromatography (column A) and identified by their infrared spectra.

Fluorination of 1H : 5H/2H : 4H-*Octafluoro*cyclo*hexane*.—The octafluoro*cyclo*hexane (8·0 g.; b. p. 125°) was passed during 20 min. over cobaltic fluoride at about 170°. Gas chromatography of the waxy product (5·7 g.) revealed six components with retention times the same as those of the compounds mentioned below. The mixture (5·0 g.) was separated by preparative-scale gas chromatography (N_2 flow-rate 9 l./hr.) to give: (i) a mixture (0·4 g.) of perfluoro*cyclo*hexane and undecafluoro*cyclo*hexane; (ii) 1*H*/2*H*-decafluoro*cyclo*hexane (0·25 g.); (iii) 1*H*/4*H*-decafluoro*cyclo*hexane (1·0 g.); (iv) 1*H* : 3*H*/-decafluoro*cyclo*hexane (0·2 g.); and (v) 1*H*/2*H* : 4*H*-nonafluoro*cyclo*hexane (0·85 g.). All these structures were verified by infrared spectroscopy.

Fluorination of 1H : 2H/4H : 5H-*Octafluoro*cyclo*hexane*.—The octafluoro*cyclo*hexane (8·0 g.; b. p. 133°) was passed during 20 min. over cobaltic fluoride at 160°. Gas chromatography of the waxy product (8·0 g.) revealed five components with retention times the same as those of compounds mentioned below. The mixture (5·0 g.) was separated by preparative-scale gas chromatography (column A; 110°, N_2 flow-rate 9 l./hr.), to give: (i) traces of perfluoro*cyclo*hexane and undecafluoro*cyclo*hexane; (ii) a mixture (2·1 g.) of 1*H*/4*H*- and 1*H*/3*H*-decafluoro*cyclo*hexane; (iii) 1*H* : 2*H*/-decafluoro*cyclo*hexane (trace); and (iv) 1*H* : 2*H*/4*H*-nonafluoro*cyclo*hexane (0·8 g.). Fractions (ii) and (iv) were identified by their infrared spectra.

Fluorination of 1H : 2H : 4H/5H-*Octafluoro*cyclo*hexane*.—The octafluoro*cyclo*hexane (7·5 g.; b. p. 136°) was passed during 20 min. over cobaltic fluoride at 160°. Gas chromatography of the waxy product (8·0 g.) (tritolyl phosphate–kieselguhr 1 : 3; 136°; N_2 flow-rate 0·9 l./hr.) revealed eleven components. The mixture (5·0 g.) was separated by preparative-scale gas chromatography (column A; 106°; N_2 flow-rate 8·6 l./hr.), to give: (i) a mixture (0·2 g.) of perfluoro*cyclo*hexane and undecafluoro*cyclo*hexane; (ii) 1*H*/2*H*-decafluoro*cyclo*hexane (trace); (iii) a mixture (0·5 g.) of 1*H*/4*H*- and 1*H*/3*H*-decafluoro*cyclo*hexane; (iv) 1*H* : 4*H*/-decafluoro*cyclo*hexane (0·1 g.); (v) 1*H* : 4*H*/2*H*-nonafluoro*cyclo*hexane (0·5 g.); (vi) 1*H* : 3*H*/-decafluoro*cyclo*hexane (0·1 g.); (vii) 1*H* : 2*H*/4*H*-nonafluoro*cyclo*hexane (0·7 g.); (viii) 1*H*/2*H* : 4*H*-nonafluoro*cyclo*hexane (0·35 g.); (ix) 1*H* : 2*H* : 4*H*/-nonafluoro*cyclo*hexane (trace); and (x) starting material (1·1 g.). Fractions (iii), (v), (vi), (vii), and (viii) had correct infrared spectra.

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