29. *Fluoro*cyclo*hexanes. Part IV.*[1] 1H : 2H/4H- *and* 1H : 2H : 4H/-*Nonafluoro*cyclo*hexane* * *and Related Compounds.*

By R. Stephens, J. C. Tatlow, and E. H. Wiseman.

Two nonafluoro*cyclo*hexanes, b. p. 107° (I) and 124° (II), isolated from the polyfluoro*cyclo*hexane mixture made by the fluorination of benzene, have been studied by methods making extensive use of gas chromatography on both analytical and preparative scales. Six unsaturated products, obtained from the isomer (I) by dehydrofluorination with aqueous alkali, were identified as *1H*-heptafluoro*cyclo*hexa-1 : 4-diene, *1H*- and *2H*-heptafluoro*cyclo*hexa-1 : 3-diene, and *1H* : *5H*-, *3H* : *4H*/-, and *4H* : *5H*/-octafluoro*cyclo*hexene. Compound (I) was thus *1H* : *2H*/*4H*-nonafluoro*cyclo*hexane; this was confirmed by further fluorination with cobaltic fluoride to the known *1H* : *2H*/-, *1H*/*3H*-, and *1H*/*4H*-decafluoro*cyclo*hexane. With alkali, compound (II) gave the same six unsaturated products, together with *1H* : *4H*-octafluoro*cyclo*hexene, and fluorination afforded the three *cis*-decafluoro-compounds: it was therefore *1H* : *2H* : *4H*/-nonafluoro*cyclo*hexane. All four *1H* : *2H* : *4H*-nonafluoro-compounds were synthesised from *4H*-nonafluoro*cyclo*hexene by addition of chlorine, followed by reduction with lithium aluminium hydride. A *cyclo*alkene, *1H* : *2H* : *4H*-heptafluoro*cyclo*hexene (b. p. 106°), was obtained in very small yield from the fraction of the polyfluoro-mixture affording compound (I).

Isolation of Compounds.—The complete characterisation of two *1H* : *2H* : *4H*-nonafluoro*cyclo*hexanes has been reported recently.[1] From the same source, the mixture of cyclic polyfluoro-compounds [1-4] obtained by the treatment of benzene in the vapour phase with cobaltic fluoride at about 150°, two new isomeric nonafluoro-compounds (I and II) and a heptafluoro*cyclo*hexene (III) have been isolated and identified. Investigations of them and various derived compounds are reported in this paper.

Two of the new compounds to be described (I and III) were contained in a major fraction, b. p. 106—107°, obtained by fractional distillation controlled by analytical gas chromatography,[5, 6] of the polyfluoro-mixture remaining after removal [1] of *1H* : *4H*/*2H*-(VII) and *1H*/*2H* : *4H*-nonafluoro*cyclo*hexane (VIII) (b. p. 92° and 101° respectively). However, this fraction, though inseparable further by fractional distillation, was shown by analytical gas chromatography to be a mixture of two components, one in considerable excess. The constituents were separated by preparative-scale gas chromatography,[7] the minor one (III) with the lower retention time being a liquid heptafluoro*cyclo*hexene (b. p. 106°) and the major component (I) a nonafluoro*cyclo*hexane (b. p. 107°, m. p. 35°).

Further distillation of the original polyfluoro*cyclo*hexane mixture having b. p. >107° yielded a major fraction of b. p. 118°, which was *1H* : *4H*/*2H* : *5H*-octafluoro*cyclo*hexane,[8, 9] and then, over the boiling range of 120—127°, a mixture of six compounds was obtained but in small yield. This could be separated [9] only by preparative-scale gas chromatography and one of the pure compounds isolated (II) had b. p. 124°, m. p. 26°, and was

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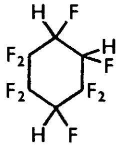
* The stereochemical nomenclature used here and in other Parts follows that suggested for the inositols (Angyal and Macdonald, *J.*, 1952, 686; Whiffen, *Chem. and Ind.*, 1956, 964). The American convention, adopted also in the *Journal* (see *J.*, 1952, 5059), governing the use of *H* to denote hydrogen in polyhalogeno-compounds contains the limitation that the ratio of hydrogen to halogen shall not " ordinarily " exceed 1 : 3. To preserve uniformity of names in the present series of papers this limitation is not applied to the relatively small proportion of compounds affected.

[1] Part III, Godsell, Stacey, and Tatlow, *Tetrahedron*, 1958, **2**, 193.
[2] Barbour, Mackenzie, Stacey, and Tatlow, *J. Appl. Chem.*, 1954, **4**, 341, 347.
[3] Smith and Tatlow, *J.*, 1957, 2505.
[4] Evans, Godsell, Stephens, Tatlow, and Wiseman, *Tetrahedron*, 1958, **2**, 183.
[5] Evans and Tatlow, *J.*, 1955, 1184.
[6] *Idem*, " Vapour Phase Chromatography," (Editor Desty), Butterworths, London, 1956, p. 256.
[7] Evans, Massingham, Stacey, and Tatlow, *Nature*, 1958, **182**, 591.
[8] Stephens and Tatlow, *Chem. and Ind.*, 1957, 821.
[9] Nield, Stephens, and Tatlow, following paper.

another nonafluoro*cyclo*hexane. This (II) and the other stereoisomeric nonafluoro-compounds (I, VII, and VIII) were all synthesised together by an alternative method (see below).

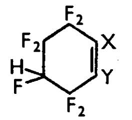
The compounds (I—III) were identified by dehydrofluorination, the mixtures of unsaturated products being separated by preparative-scale gas chromatography. The columns used before [5, 6] and a larger unit [7] were used, the latter, a tube 16 ft. × 7·5 cm. being capable of handling charges of 10—25 g. of most mixtures. The dehydrofluorination products were characterised by oxidation and further dehydrofluorination. Considerable use was also made of infrared spectroscopy, not only for proving the identity of known compounds with authentic samples, but also for confirmation of the types of double bond (Burdon and Whiffen [10]) and $\geqslant$CH groups (Steele and Whiffen [11]) present.

*Characterisation of the Heptafluoro*cyclo*hexene of b. p.* 106°.—This substance (III), the minor constituent of the fraction of b. p. 106—107°, was shown by analysis to have the formula $C_6H_3F_7$, and was the first unsaturated compound to be found in the product of the benzene–cobaltic fluoride reaction. It was oxidised by aqueous potassium permanganate to the known 3*H*-heptafluoroadipic acid,[2, 5, 13] and had an infrared spectrum consistent [10, 11] with the presence of a $>$CH=CH$<$ double bond and a hydrogen substituent on the β-carbon atom. Dehydrofluorination of this olefin (III) afforded a mixture, which was shown by analytical gas chromatography to contain two compounds (IX and XI). These were isolated by preparative-scale gas chromatography, each being a new hexafluoro*cyclo*hexadiene. Oxidation was carried out with potassium permanganate in dry acetone, which converts [12] fluoro-olefins into carboxylic acids smoothly and rapidly. Difluoromalonic acid was obtained from one diene (IX) and tetrafluorosuccinic acid from the other (XI). Ultraviolet and infrared spectra confirmed the presence of a 1 : 4-diene system in (IX) and a 1 : 3-diene system in (XI), both with two hydrogen atoms carried on one double bond. Thus, the parent olefin (III) must have been 1*H* : 2*H* : 4*H*-heptafluoro*cyclo*hexene, and the derived dienes were 1*H* : 2*H*-hexafluoro*cyclo*hexa-1 : 4- (IX) and -1 : 3-diene (XI).



(I) 1*H*a: 2*H*e/4*H*a

(II) 1*H*e: 2*H*a: 4*H*a/

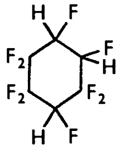


(III) X = Y = H

(IV) X = F, Y = H

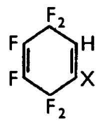
(V) X = Y = F

(VI) X = H, Y = F



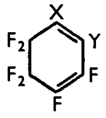
(VII) 1*H*a: 4*H*e/2*H*a

(VIII) 1*H*a/2*H*a: 4*H*a



(IX) X = H

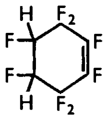
(X) X = F



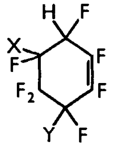
(XI) X = Y = H

(XII) X = H, Y = F

(XIII) X = F, Y = H

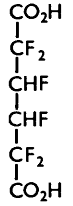


(XIV) 4*H*:5*H*/

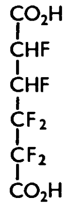


(XV) X = H, Y = F 3*H*:4*H*/

(XVI) X = F, Y = H



(XVII)



(XVIII)

The *cyclo*hexene (III) had been reported before by Fear and Thrower [13] as one of the major products of the fluorination of benzene with manganese trifluoride. This fluorination was repeated by us, and the previous results confirmed: the product obtained was identical

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[10] Burdon and Whiffen, *Spectrochim. Acta*, 1958, **12**, 139.

[11] Steele and Whiffen, *Tetrahedron*, 1958, **3**, 181.

[12] Burdon and Tatlow, *J. Appl. Chem.*, 1958, **8**, 293.

[13] Fear and Thrower, *ibid.*, 1955, **5**, 353; Fear, Thrower, and Veitch, *ibid.*, p. 589.

with that from the reaction with cobaltic fluoride. Manganese trifluoride provides the easier route to the compound.

*Characterisation of the Nonafluoro*cyclo*hexane of b. p.* 107°.—The substance (I) was dehydrofluorinated with aqueous potassium hydroxide under comparatively mild conditions (contrast the known[1] isomers), and gave a mixture which was shown by analytical gas chromatography to contain, besides a little starting material, six products (IV, X, XII—XV), which were isolated pure by preparative-scale gas chromatography. The first three to emerge from the column were dienes and had gas-chromatographic retention times and infrared spectra identical with those of 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene (X) and 1*H*- and 2*H*-heptafluoro*cyclo*hexa-1 : 3-diene (XII and XIII) respectively. These were characterised in the earlier work,[1] but for the conjugated dienes it was not possible to distinguish between the two compounds (b. p. 72° and 76°) obtained. Though each could have had either formula (XII) or formula (XIII), and no other, it was impossible at that stage to allocate the structures more precisely.

An attempt was made to decide between the two possibilities by controlled addition of fluorine to each of the dienes by passage over cobaltic fluoride at only slightly elevated temperatures. This had been attempted previously[1] but the products were not then identified conclusively. By normal 1 : 2- and 1 : 4-additions, only the 1*H*-1 : 3-diene should give 4*H*-nonafluoro*cyclo*hexene (V) among the *cyclo*hexene products, but it appeared to be formed together with unidentified substances from both. When the reactions were repeated, the lower-boiling 1 : 3-diene (b. p. 72°) was passed over cobaltic fluoride at 55—65° in the small static reaction vessel described before,[4] to give a mixture of seven compounds. These were separated gas-chromatographically and identified by retention times and by infrared spectroscopy as perfluoro*cyclo*hexane, decafluoro*cyclo*hexene, undecafluoro*cyclo*hexane, 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene (X), and 1*H*-, 3*H*-, and 4*H*- (V) nonafluoro*cyclo*hexene. The isomeric 1 : 3-diene of b. p. 76° gave a very similar pattern of products, only decafluoro*cyclo*hexene being absent. Thus, the 4*H*-*cyclo*hexene (V) was in fact formed in both cases, as was a 1 : 4-diene (X). Clearly, no progress had been made in elucidating the structures of the 1 : 3-dienes and a new problem had been posed. However, other work[14] in this Department has since shown that, when brought into contact with metals or metallic fluorides at elevated temperatures, cyclic fluoro-1 : 3- and -1 : 4-dienes are interconverted: possibly equilibria are established. It seems that in the cobaltic fluoride vessel some of the 1 : 3-diene must rearrange thus to the 1 : 4-isomer by contact with a metallic fluoride (copper fluoride in the preheating system or nickel or cobalt fluoride near the inlet) before being saturated with fluorine. Additions to the mixture of 1 : 3- and 1 : 4-dienes can then give all the other products found.

The fourth product (IV) of the original dehydrofluorination was an octafluoro*cyclo*hexene. On oxidation with permanganate in acetone, the known 3*H*-heptafluoroadipic acid was obtained. Infrared spectroscopy also indicated the presence of a $>$CH=CF$<$ double bond, and of hydrogen at the β-position. Reaction with cobaltic fluoride in the small static reaction vessel gave two decafluoro*cyclo*hexanes, shown by gas chromatography and infrared spectroscopy to be the 1*H*/3*H*- and 1*H* : 3*H*/-isomers. The structure of the product (IV) was thus established as 1*H* : 5*H*-octafluoro*cyclo*hexene.

The isolation of this compound (IV) enabled the structures of the two conjugated dienes (XII and XIII), mentioned above, to be unequivocally allocated. On dehydrofluorination, by normal elimination processes it can give only two dienes, 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene (X) and 2*H*-heptafluoro*cyclo*hexa-1 : 3-diene (XIII). Experimentally, the *cyclo*hexene (IV) reacted only slowly with aqueous alkali but gave two products, the first being the unconjugated diene (X). The other was identical with the conjugated diene of longer gas-chromatographic retention time and higher boiling point (76°), which must therefore be the 2*H*-compound (XIII).

The fifth product (XIV) of the dehydrofluorination of compound (I) was also an

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[14] Gething, Patrick, and Tatlow, unpublished observations.

octafluoro*cyclo*hexene. Oxidation of it afforded a hexafluoroadipic acid which was degraded by aqueous alkaline potassium permanganate to difluoromalonic acid and so it had a 3*H* : 4*H*-structure (XVII). Dehydrofluorination of the parent (XIV) with alkali gave the 1*H*-1 : 4-diene (X) and hexafluorobenzene. Infrared spectroscopy confirmed the presence of a $>CF=CF<$ group and the absence of an α-hydrogen atom and so the compound (XIV) must have been a 4*H* : 5*H*-octafluoro*cyclo*hexene. However, it differed from the known [1] 4*H*/5*H*-compound, and the derived acid (XVII) differed from (±)-3*H* : 4*H*-hexafluoroadipic acid.[1] The compound (XIV) must therefore have been the 4*H* : 5*H*/-isomer (it was dehydrofluorinated more readily than the 4*H*/5*H*-compound). This was confirmed in two ways. First, attempts to resolve the dibrucine salt of the derived hexafluoroadipic acid (XVII) were unsuccessful. Secondly, reaction of the *cyclo*hexene (XIV) with cobaltic fluoride afforded only undeca- and 1*H* : 2*H*/-deca-fluoro*cyclo*hexane.[3,4] Compound (XIV) was therefore 4*H* : 5*H*/-octafluoro*cyclo*hexene and the derived acid (XVII) was *meso*-3*H* : 4*H*-hexafluoroadipic acid.

The sixth product obtained from the dehydrofluorination of the nonafluoro*cyclo*hexane (I) was an octafluoro*cyclo*hexene (XV) to which fluorine was added by cobaltic fluoride giving 1*H* : 2*H*/-decafluoro*cyclo*hexane.[3,4] Oxidation of the *cyclo*hexene (XV) gave a hexafluoroadipic acid (XVIII). This acid was degraded by aqueous alkaline permanganate to tetrafluorosuccinic acid, but it differed from the known [1] (±)-*threo*-2*H* : 3*H*-hexafluoroadipic acid. The compound (XV) was therefore 3*H* : 4*H*/-octafluoro*cyclo*hexene (infrared spectroscopy confirmed the $>CF=CF<$ group and the presence of hydrogen α and β to it), and the acid (XVIII) was (±)-*erythro*-2*H* : 3*H*-hexafluoroadipic acid. Dehydrofluorination of the *cyclo*hexene (XV) gave a mixture shown by analytical gas chromatography to contain 5 components, one of them starting material. Three others were the 1*H*- and 2*H*-1 : 3-dienes (XII) and (XIII) (arising from 1 : 2-elimination) and hexafluorobenzene [arising from a 1 : 4-elimination of hydrogen and fluorine as expected from the structure of compound (XV)]. The fourth product was formed in too small quantity for conclusive proof of its structure: preliminary experiments indicate that it is a 3*H* : 6*H*-octafluoro*cyclo*hexene (XVI) which could be formed from the 3*H* : 4*H*/-compound (XV) by a prototropic change. If this is true it is the first example of such an effect in fluoro*cyclo*hexanes. It is also of interest that this *cyclo*hexene (XV) has an abnormally long retention time in gas chromatography, even for a compound with a *cis*-1*H* : 2*H*-arrangement:[4] it is retained much longer than the 4*H* : 5*H*/-isomer (XIV) (cf. the 3*H*/4*H*- and 4*H*/5*H*-analogues [1]). The refractive index of compound (XV) is also high, and the association of *cis*-1 : 2-hydrogen and an adjacent double bond obviously gives rise to abnormal properties.

The structures established as described above for each of the products of dehydrofluorination of the nonafluoro*cyclo*hexane (I) showed that it had hydrogen at positions 1, 2, and 4. Without profound rearrangements, a 1*H* : 2*H* : 3*H*-compound could not give rise to the 1 : 4-diene (X) or the 4*H* : 5*H*-ene (XIV), whilst from a 1*H* : 3*H* : 5*H*-structure none of the products should be obtained.

Further, in both of the *cyclo*hexenes (XIV) and (XV), the 1*H* : 2*H*-system was proved conclusively to be *cis*, since the only product of saturation of the double bonds by fluorine was the known 1*H* : 2*H*/-decafluoro*cyclo*hexane. Hence, if it is assumed that in the more stable conformation of a *cyclo*hexane of this general type, the hydrogen atoms, being smaller, preferentially occupy *axial* positions where possible,[3] the nonafluoro-compound (I) could only be either the 1*H*a : 2*H*e/4*H*a- or the 1*H*e : 2*H*a : 4*H*a/-stereoisomer. In the cases of the two nonafluoro-compounds (VII) and (VIII) with 1*H*a/2*H*a-systems, studied earlier,[1] monounsaturated compounds were formed only from eliminations at the isolated hydrogen atom, even when this was *equatorial*, and in both cases elimination was relatively slow. This paralleled the difficulty in dehydrofluorination [3] of 1*H*/2*H*-decafluoro*cyclo*hexane compared with that of its five isomers. The 1*H* : 2*H*/-decafluoro-analogue however was dehydrofluorinated at a rate qualitatively comparable [3,4] with those of compounds possessing a $>CHF$ group (with an *axial* hydrogen) flanked by two $>CF_2$ groups. This is to be expected; it seems likely that the arrangement $>CF_2{\cdot}CHF{\cdot}CHF{\cdot}CF_2<$ has hydrogen atoms which are less acidic than the one in $>CF_2{\cdot}CHF{\cdot}CF_2<$, but that fluorine in the group $>CHF$ is rather less tightly bound than in $>CF_2$. If the preferred bimolecular *trans*-elimination[15] can operate entirely within the system $>CHF{\cdot}CHF<$ to give $>CH{=}CF<$, as in the case of the *cis*-1*H* : 2*H*-decafluoro-compound, the reactivity is then qualitatively comparable with that of $>CF_2{\cdot}CHF{\cdot}CF_2<$ since both effects are involved and roughly cancel out. With the *trans*-1*H* : 2*H*-isomer however the preferred process can only occur " outwards," *i.e.*, the fluorine must come from the more stable group ($>CF_2$), so that the overall reactivity is lowered. Alternatively, the " inwards " elimination can proceed by a less favoured mechanism. In either case elimination from the 1*H*/2*H*-system should occur only slowly.

With 1*H* : 2*H* : 4*H*-nonafluoro*cyclo*hexanes possessing *cis*-1*H* : 2*H*-systems, it appears from the foregoing discussion that, upon dehydrofluorination, *cyclo*hexenes should be obtained by relatively easy eliminations, the hydrogen coming from either the 4- or the 1 : 2-positions. Experimentally, from compound (I), elimination of hydrogen from $C_{(4)}$ occurred in both possible directions, to give two olefins with $>CF{=}CF<$ double bonds (XIV and XV) (in all *ca.* 65% of the monounsaturated dehydrofluorination products), but elimination from the 1 : 2-positions occurred in only one direction, to give exclusively the 1*H* : 5*H*-*cyclo*hexene (IV) (*ca.* 35%). The reactions were qualitatively more rapid than for the *trans*-1*H* : 2*H*-stereoisomers.[1] This suggested strongly that the hydrogen on position 2 of the parent compound (I), being the one retained in the only elimination from the 1 : 2-system, was *equatorial*. Therefore, the precursor (I) was 1*H*a : 2*H*e/4*H*a-nonafluoro*cyclo*hexane.

This allocation of structure was confirmed completely by further fluorination of the fluorohydrocarbon (I) with cobaltic fluoride. Three known decafluoro*cyclo*hexanes were obtained, identical with authentic specimens.[4] They were the 1*H* : 2*H*/- (b. p. 91°), the 1*H*/4*H*- (b. p. 78°), and the 1*H*/3*H*-isomer (b. p. 78°).

*Characterisation of the Nonafluoro*cyclo*hexane of b. p.* 124°.—There should be four stereoisomeric 1*H* : 2*H* : 4*H*-nonafluoro*cyclo*hexanes, and the remaining one was isolated first from a synthesis which gave all four together. 4*H*-Nonafluoro*cyclo*hexene (V), a product[4, 5] of the dehydrofluorination of 1*H* : 3*H*- and 1*H* : 4*H*-decafluoro*cyclo*hexanes, was treated with chlorine under ultraviolet irradiation. The adduct was not isolated, but was reduced directly with lithium aluminium hydride in diethyl ether, which readily replaces[16, 17] chlorine in a chlorofluorocarbon by hydrogen. The product was shown by analytical gas chromatography to contain four components, which were isolated pure by preparative-scale gas chromatography. They were, in order of emergence from the column, the known nonafluoro*cyclo*hexanes 1*H* : 4*H*/2*H* (b. p. 92°; VII), 1*H* : 2*H*/4*H* (b. p. 107°; I), 1*H*/2*H* : 4*H* (b. p. 101°; VIII), and a new compound (b. p. 124°; II). The last was shown by infrared spectroscopy to be identical with the material subsequently isolated in small amounts as described earlier from a minor fraction of the polyfluoro*cyclo*hexane mixture. It is of interest, that as in the analogous reactions[3] with decafluoro*cyclo*hexene, the major part of the hydrofluorocarbon product had the *cis*-1*H* : 2*H*-arrangement. This suggests again a predominantly *cis*-addition of chlorine and retention or inversion of configuration in the reduction by lithium aluminium hydride.

That this compound (II) had the expected 1*H* : 2*H* : 4*H*/-configuration was proved by further fluorination with cobaltic fluoride. Three decafluoro*cyclo*hexanes were obtained, and were shown to be the known[4] 1*H* : 2*H*/- (b. p. 91°), 1*H* : 3*H*/- (b. p. 89°), and 1*H* : 4*H*/-isomer (b. p. 86°). Dehydrofluorination of the 1*H* : 2*H* : 4*H*/-nonafluoro-compound (II) was carried out also, and gave seven products which were isolated by gas chromatography. Six of them were the same compounds (IV, X, XII—XV) as had been obtained from the

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[15] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 419.

[16] Tatlow and Worthington, *J.*, 1952, 1251.

[17] Roylance, Tatlow, and Worthington, *J.*, 1954, 4426.

dehydrofluorination of the stereoisomeric nonafluoro-compound (I). The seventh was another octafluoro*cyclo*hexene (VI), which was identified by oxidation and addition of fluorine. The former reaction afforded the well-known 3*H*-heptafluoroadipic acid, infrared spectroscopy confirming the presence of a $>$CH=CF$<$ double bond. By reaction with cobaltic fluoride to saturate this bond, two known[4] decafluoro*cyclo*hexanes were formed. They were the 1*H*/4*H*- and the 1*H* : 4*H*/-isomer. Compound (VI) must therefore have been 1*H* : 4*H*-octafluoro*cyclo*hexene. Fear and Thrower[13] had previously isolated this from the reaction of benzene with manganic fluoride. They had shown that it was either 1*H* : 5*H*- (IV) or 1*H* : 4*H*-octafluoro*cyclo*hexene (VI) (or a mixture of the two). From the fluorination with manganese trifluoride mentioned above we also obtained their compound. It was different from the 1*H* : 5*H*-isomer (IV) described earlier, but was now shown to be identical with the 1*H* : 4*H*-*cyclo*hexene (VI). Dehydrofluorination of this product (VI) provided the final proof of the structures of the dienes (XII and XIII), since there were obtained, in accordance with the earlier results, the 1 : 4-diene (X) and the conjugated diene of lower gas-chromatographic retention time and with b. p. 72°, identical with compound (XII) described earlier.

It is at first sight curious that, whereas the nonafluoro-compound (I) gives exclusively 1*H* : 5*H*-octafluoro*cyclo*hexene (IV) by elimination of hydrogen fluoride from positions 1 and 2, the stereoisomer (II) affords both 1*H* : 4*H*- (VI) and 1*H* : 5*H*- (IV) *cyclo*hexene in comparable amounts. In both cases reaction occurred under mild conditions. The absence of olefin (VI) from the dehydrofluorination products of the nonafluoride (I) makes the direct elimination of *equatorial* hydrogen very unlikely, whilst its behaviour on further reaction with alkali rules out the possibility that it might be formed exclusively from compound (II) and itself rearrange to give olefin (IV).

Because of their relative atomic sizes, comparatively small non-bonded interactions can be introduced into *cyclo*hexane derivatives in which fluorine progressively replaces hydrogen (there can be little overall strain in perfluoro*cyclo*hexane). However, on general conformational grounds, one form (1*H*a : 2*H*e/4*H*a) of the nonafluoro-compound (I) should be more stable than the other (1*H*e : 2*H*a/4*H*e), since presumably 1a : 3a F–F interactions, of which the latter has more, introduce most strain. However, in the case of isomer (II), the two conformations (1*H*e : 2*H*a : 4*H*a and 1*H*a : 2*H*e : 4*H*e) differ much less in their total interactions, so that they should have approximately equal stabilities. These conclusions are in accordance with the experimental results. Isomer (I) gives the *cyclo*hexene (IV) by an orthodox *trans*-elimination, the hydrogen retained being the original equatorial one, whilst from isomer (II) each of the two nearly equivalent forms gives rise to its own (different) *cyclo*hexene.

EXPERIMENTAL

Characterisation of Acids obtained as Oxidation Products.—*cyclo*Hexenes were oxidised[12] to acids by potassium permanganate in acetone. The known acids difluoromalonic,[18] tetrafluorosuccinic,[18,19] and 3*H*-heptafluoroadipic[5] were characterised as dianilinium and di-(*S*-benzylthiuronium) salts. Each sample had a correct elemental analysis and the m. p. was within 2° of the reported value. The yields quoted are those of the analytically pure salts.

Gas Chromatography.—Analytical work was carried out in columns 2 m. long × 4 mm. diameter packed with dinonyl phthalate–kieselguhr (1 : 2) and run at 93° with a nitrogen flow rate of 1·1 l./hr. In preparative-scale work two columns were used. Column A was 488 cm. long × 30 mm. diameter and was similarly packed; it was normally run at 100° with a nitrogen flow rate of 10 l./hr. Column B was 488 cm. long × 75 mm. diameter; it had the same packing and was run at 100° with a nitrogen flow rate of 49 l./hr. After preparative-scale separations each fraction obtained was distilled from the trap *in vacuo.*

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[18] Evans and Tatlow, *J.*, 1954, 3779.
[19] Buxton and Tatlow, *J.*, 1954, 1177.

Infrared Measurements.—These were made in the vapour state in a 10·1 cm. cell over the range 650—3500 cm.$^{-1}$ with a Perkin-Elmer double-beam spectrometer with rock-salt prisms. The spectra for the new compounds described have been deposited in the Documentation of Molecular Spectra issued by Butterworths.

Isolation of 1H : 2H/4H- *and* 1H : 2H : 4H/-*Nonafluoro*cyclo*hexane and* 1H : 2H : 4H-*Heptafluoro*cyclo*hexene.*—Fractional distillation controlled by analytical gas chromatography of the partly fluorinated *cyclo*hexane mixture having b. p. >101° gave a fraction with b. p. 106—107° (*ca.* 5% of the original polyfluorinated mixture), which was resolved by analytical gas chromatography into two components. Separation of the mixture (4·0 g.) in the preparative-scale gas chromatography column A afforded: (i) 1*H* : 2*H* : 4*H*-heptafluoro*cyclo*hexene (0·12 g.), b. p. 106°, n_D^{21} 1·3362 (Found: C, 34·9; H, 1·5. Calc. for $C_6H_3F_7$: C, 34·6; H, 1·45%), for which Fear and Thrower[13] gave b. p. 105—106°, n_D^{20} 1·335; and (ii) 1H : 2H/4H-*nonafluoro*cyclo*hexane* (3·60 g.), b. p. 107°, m. p. 34—35°, n_D^{44} 1·3090 (Found: C, 29·5; H, 1·3; F, 69·2. $C_6H_3F_9$ requires C, 29·3; H, 1·2; F, 69·5%).

After removal of material of b. p. 107·5—120°, mainly 1*H* : 4*H*/2*H* : 5*H*-octafluoro*cyclo*hexane,[9] b. p. 118°, there followed a mixed intermediate fraction, b. p. 120—127° (*ca.* 0·5% of the original mixture). From this there was isolated by preparative-scale gas chromatography as described elsewhere,[9] 1H : 2H : 4H/-*nonafluoro*cyclo*hexane*, b. p. 124°, m. p. 24—26°, n_D^{29} 1·3231 (Found: C, 29·7; H, 1·3%).

The 1*H* : 2*H*/4*H*-isomer gave peak No. 10 in the table of gas-chromatography results given earlier.[3] The 1*H* : 2*H* : 4*H*/-isomer, being a very small component and of long retention time under the conditions used, was not shown.

Dehydrofluorination of 1H : 2H : 4H-*Heptafluoro*cyclo*hexene.*—The olefin (3·52 g.; b. p. 106°), potassium hydroxide (15 g.), and water (15 c.c.) were boiled together for 4 hr. The organic phase (2·69 g.) was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography showed 3 peaks. Separation in the preparative-scale column A afforded: (i) 1H : 2H-*hexafluoro*cyclo*hexa*-1 : 4-*diene* (1·14 g.), b. p. 83—84°, n_D^{19} 1·3417 (Found: C, 38·4; H, 1·4. $C_6H_2F_6$ requires C, 38·3; H, 1·1%): (ii) 1H : 2H-*hexafluoro*cyclo*hexa*-1 : 3-*diene* (0·64 g.), n_D^{22} 1·3529 (Found: C, 38·3; H, 1·1%); which decomposed rapidly in air; and (iii) 1*H* : 2*H* : 4*H*-heptafluoro*cyclo*hexene (0·63 g.), b. p. 106°. By longer refluxing it was possible to destroy all the parent *cyclo*hexene.

Characterisation of 1H : 2H-*Hexafluoro*cyclo*hexa*-1 : 4-*diene.*—(a) *Oxidation.* The diene (0·54 g.; b. p. 83—84°), potassium permanganate (2 g.), and dry acetone (400 c.c.), shaken together at room temperature for ½ hr., yielded difluoromalonic acid (78%).

(b) *Spectroscopy.* The diene showed two infrared $\gt C{=}C\lt$ bands (1688 and 1770 cm.$^{-1}$), suggesting two hydrogen atoms on one double bond of a 1 : 4-diene. A $\geqslant$C–H band at 3087 cm.$^{-1}$ was due to =C–H only. No selective ultraviolet absorption was shown in the range 2400—3000 Å.

Characterisation of 1H : 2H-*Hexafluoro*cyclo*hexa*-1 : 3-*diene.*—(a) *Oxidation.* The diene (0·29 g.), oxidised with potassium permanganate (1 g.) in dry acetone (200 c.c.), afforded tetrafluorosuccinic acid (60%).

(b) *Spectroscopy.* Two $\gt C{=}C\lt$ bands were shown in the infrared spectrum, at 1734 and 1635 cm.$^{-1}$. In the ultraviolet region there was a band at 2520 Å (ε ~6300) (0·57 g./l. in ether).

Other Reactions of 1H : 2H : 4H-*Heptafluoro*cyclo*hexene.*—(a) *Oxidation.* The compound (5·62 g.; b. p. 106°), potassium permanganate (12 g.), and water (50 c.c.) were boiled together for 23 hr. Isolation as usual yielded 3*H*-heptafluoroadipic acid, which was characterised as the dianilinium salt (7·33 g.).

(b) *Spectroscopy.* The compound showed a characteristically[10] very weak –HC=CH– infrared band at 1682 cm.$^{-1}$ and a $\geqslant$C–H band at 2981 cm.$^{-1}$ typical of β-hydrogen. No selective ultraviolet absorption was shown in the range 2400—3000 Å.

Dehydrofluorination of 1H : 2H/4H-*Nonafluoro*cyclo*hexane.*—The nonafluoro-compound (50·0 g.; b. p. 107°), potassium hydroxide (50·0 g.), and water (75 c.c.) were shaken together at 15° for 7 hr. The organic phase (41·6 g.) was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography showed 7 peaks. Separation of part of the mixture (17·50 g.) in the large preparative-scale gas chromatography column B afforded: (A) 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene (0·05 g.); (B) 1*H*-heptafluoro*cyclo*hexa-1 : 3-diene (0·02 g.); (C) 2*H*-heptafluoro*cyclo*hexa-1 : 3-diene (0·03 g.); (D) 1*H* : 5*H*-*octafluoro*cyclo*hex*-1-*ene* (4·65 g.), b. p. 85°, n_D^{21} 1·3260 (Found: C, 32·1; H, 1·0. $C_6H_2F_8$ requires C, 31·9; H, 0·9%); (E)

4*H* : 5*H*/-*octafluoro*cyclo*hexene* (2·55 g.), b. p. 99°, n_D^{21} 1·3234 (Found: C, 32·0; H, 0·9; F, 66·8. $C_6H_2F_8$ requires C, 31·9; H, 0·9; F, 67·2%); (F) unchanged 1*H* : 2*H*/4*H*-nonafluoro*cyclo*hexane (0·55 g.); and (G) 3H : 4H/-*octafluoro*cyclo*hexene* (6·01 g.), b. p. 116°, n_D^{21} 1·3390 (Found: C, 32·3; H, 1·0; F, 66·8%). The relative proportions of the products were varied by alteration of the reaction conditions, more vigorous treatment removing all starting material and increasing the amounts of products (A)—(C) at the expense of (F) and (G). Small quantities of hexafluorobenzene[20] were formed also from these *cyclo*hexenes. Compound (D) was relatively resistant to further dehydrofluorination except under drastic conditions.

Products (A), (B), and (C) had infrared spectra respectively identical with those of the dienes (i), (ii), and (iii) obtained[1] by dehydrofluorination of 1*H* : 4*H*/2*H*- and 1*H*/2*H* : 4*H*-nonafluoro*cyclo*hexane.

Characterisation of 1H : 5H-*Octafluoro*cyclo*hexene*.—(a) *Oxidation*. This compound (0·53 g.; b. p. 85°), oxidised by potassium permanganate (0·40 g.) in dry acetone (100 c.c.), gave 3*H*-heptafluoroadipic acid (54%).

(b) *Dehydrofluorination*. The *cyclo*hexene (2·31 g.), potassium hydroxide (10 g.), and water (10 c.c.) were boiled together for 7 hr. After being washed with water and dried ($MgSO_4$), the product (1·37 g.) showed 3 peaks in analytical gas chromatography, with retention times identical with those of 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene, 2*H*-heptafluoro*cyclo*hexa-1 : 3-diene, and unchanged starting material, respectively. Separation in the preparative-scale column A (temp. 96°, N_2 flow-rate 9·6 l./hr.) gave the 1*H*-1 : 4-diene (0·61 g.), the 2*H*-1 : 3-diene (b. p. 76°) (0·28 g.), and unchanged 1*H* : 5*H*-*cyclo*hexene (0·24 g.). These three compounds had infrared spectra identical with those of the samples A, C, and D, respectively, described above. The 2*H*-1 : 3-diene was identical also with compound (iii) obtained[1] by dehydrofluorination of 1*H* : 4*H*/2*H*- and 1*H*/2*H* : 4*H*-nonafluoro*cyclo*hexane.

(c) *Fluorination*. The *cyclo*hexene (4·5 g.) was fluorinated by passage through the small static cobaltic fluoride reaction vessel.[4] It was introduced from a micro-burette and carried through (temp. 60—65°) in a stream of nitrogen (flow rate 5 l./hr.). The products were condensed from the nitrogen stream in a trap cooled by solid carbon dioxide. Analytical gas chromatography of the product (4·70 g.) showed 4 peaks with retention times the same as those of the compounds named below. Separation in the preparative-scale column A yielded: (i) dodecafluoro*cyclo*hexane (0·11 g.); (ii) undecafluoro*cyclo*hexane (2·02 g.); (iii) 1*H*/3*H*-decafluoro*cyclo*hexane (1·46 g.); and (iv) 1*H* : 3*H*/-decafluoro*cyclo*hexane (0·60 g.). These compounds had infrared spectra identical with those of authentic specimens.[4]

(d) *Spectroscopy*. The *cyclo*hexene had a –HC=CF– infrared band at 1717 cm.$^{-1}$, and $\geqslant$C–H bands at 3102, 3067, and 2980 cm.$^{-1}$, but there was no selective ultraviolet absorption between 2400 and 3000 Å.

Characterisation of 4H : 5H/-*Octafluoro*cyclo*hexene*.—(a) *Oxidation*. The olefin (3·78 g.; b. p. 99°) was oxidised with potassium permanganate (7·68 g.) in dry acetone (750 c.c.), to give an acidic solid (3·88 g.). Distillation of a portion (0·19 g.) at 160° (bath-temp.)/0·5 mm. on to a cold finger gave the very hygroscopic meso-3H : 4H-*hexafluoroadipic acid* (0·11 g.), m. p. 163—165° (Found: C, 28·3; H, 1·8. $C_6H_4O_4F_6$ requires C, 28·4; H, 1·6%). The acid gave a *dianilinium salt* (60%) (from acetone–chloroform), m. p. 200—201° (Found: C, 48·7; H, 4·0%; equiv., 220. $C_{18}H_{18}O_4N_2F_6$ requires C, 49·1; H, 4·1%; equiv., 220), and a *di*-(S-*benzylthiuronium*) *salt* (71%) (from water), m. p. 228—229° [depressed in admixture with the salt of the (±)-acid] (Found: C, 45·5; H, 4·2; F, 19·2. $C_{22}H_{24}O_4N_4S_2F_6$ requires C, 45·0; H, 4·1; F, 19·4%).

(b) *Fluorination*. The *cyclo*hexene (3·6 g.) was passed through the small static cobaltic fluoride reaction vessel (temp. 50°) in nitrogen (flow-rate 5 l./hr.). The product (2·0 g.) was isolated as previously, and analytical gas chromatography showed that it contained two components. Separation in the preparative-scale column A afforded undecafluoro*cyclo*hexane (0·9 g.) and 1*H* : 2*H*/-decafluoro*cyclo*hexane[3, 17] (0·7 g.). The last compound had the correct infrared spectrum.

(c) *Dehydrofluorination*. The olefin (0·81 g.), potassium hydroxide (4 g.), and water (5 c.c.) were boiled together for 3½ hr. The product was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography showed two components with retention times corresponding to those of 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene and hexafluorobenzene. Separation (0·29 g.) by preparative-scale gas chromatography yielded the 1 : 4-diene

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[20] Godsell, Stacey, and Tatlow, *Nature*, 1956, **178**, 199.

(0·18 g.) and hexafluorobenzene[20] (0·05 g.). These two compounds had correct infrared spectra.

(d) *Spectroscopy.* The olefin had an –FC=CF– absorption band at 1750 cm.$^{-1}$ and $\geqslant$C–H bands at 2979 and 2975 cm.$^{-1}$, the last two characteristic of hydrogen on carbon β to the olefinic group. There was no selective ultraviolet absorption.

Oxidation of meso-3H : 4H-*Hexafluoroadipic Acid.*—The acid (3·30 g.), potassium permanganate (10 g.), potassium hydroxide (10 g.), and water (150 c.c.), refluxed together for 16 hr., yielded difluoromalonic acid (73%).

Attempted Optical Resolution of meso-3H : 4H-*Hexafluoradipic Acid.*—The acid (2·53 g.) in ethanol (25 c.c.) was added to a solution of (–)-brucine (7·85 g.) in ethanol (125 c.c.). The mixture was kept for 10 min. and then evaporated to dryness. The solid (9·89 g.) was twice recrystallised from water, to yield the *dibrucine salt* (30% recovery), m. p. 205—207° (Found: C, 59·4; H, 5·4. $C_{52}H_{56}O_{12}N_4F_6$ requires C, 59·9; H, 5·4%).

Repeated recrystallisation of this salt did not change the optical rotatory power, and specimens of acid isolated from various crops all had m. p. and mixed m. p. 163—164° and were optically inactive. Their infrared spectra were identical with each other, and were different from those[1] of (+)- and (–)-3*H* : 4*H*-hexafluoroadipic acid and their racemate.

Characterisation of 3H : 4H/-*Octafluoro*cyclo*hexene.*—(a) *Oxidation.* The compound (3·22 g.; b. p. 116°) was oxidised with potassium permanganate (6·00 g.) in dry acetone (700 c.c.) and gave an acidic solid (2·86 g.). Distillation of a sample (0·21 g.) at 135° (bath-temp.)/0·1 mm. on to a cold finger gave the very hygroscopic (±)-erythro-2H : 3H-*hexafluoroadipic acid* (0·16 g.), m. p. 107—109° (Found: C, 27·7; H, 1·4%; equiv., 123. $C_6H_4O_4F_6$ requires C, 28·4; H, 1·6%; equiv., 127). The crude acid in ether was treated with aniline to give *dianilinium* 2H : 3H-*hexafluoroadipate* (60% overall), m. p. 169—171° (from acetone–chloroform) (Found: C, 49·1; H, 4·1; F, 25·9. $C_{18}H_{18}O_4N_2F_6$ requires C, 49·1; H, 4·1; F, 25·9%). The dianilinium salt (0·36 g.) in water with *S*-benzylthiuronium chloride gave the *di*-(S-*benzylthiuronium*) *salt* (0·29 g.), m. p. 216—217° (from water) (Found: C, 45·0; H, 4·1; F, 19·5%).

(b) *Fluorination.* The olefin (3·3 g.), fluorinated as before in the small static cobaltic fluoride vessel,[4] yielded a product (2·60 g.), a sample (0·43 g.) of which was separated in the preparative-scale column A (temp. 80°) to give (i) undecafluoro*cyclo*hexane (0·09 g.) and (ii) 1H : 2H/-decafluoro*cyclo*hexane (0·18 g.). These compounds had correct infrared spectra.

(c) *Dehydrofluorination.* The *cyclo*hexene (40·4 g.), potassium hydroxide (41 g.), and water (145 c.c.) were boiled together for 2 hr. The organic layer (containing 29·4 g.) was separated, washed with water, and dried ($MgSO_4$). Examination by analytical gas chromatography showed the presence of 5 components. Separation (27·6 g.) in the preparative-scale column B gave: (i) 1*H*-heptafluoro*cyclo*hexa-1 : 3-diene (4·1 g.); (ii) 2*H*-heptafluoro*cyclo*hexa-1 : 3-diene (9·7 g.); (iii) hexafluorobenzene (0·4 g.); (iv) (suspected) 3*H* : 6*H*-octafluoro*cyclo*hexene (0·1 g.); and (v) unchanged 3*H* : 4*H*/-octafluoro*cyclo*hexene (9·9 g.). Fractions (i), (ii), (iii), and (v) had correct infrared spectra.

(d) *Spectroscopy.* The *cyclo*hexene had a –FC=CF– infrared band at 1746 cm.$^{-1}$ and $\geqslant$C–H bands at 2979 and 2960 cm.$^{-1}$, characteristic of hydrogen on carbons respectively β and α to the olefinic group. No selective absorption was shown between 2400 and 3000 Å.

Oxidation of (±)-erythro-2H : 3H-*Hexafluoroadipic Acid.*—The acid (0·75 g.) was refluxed with potassium permanganate (2·50 g.), potassium hydroxide (2·50 g.), and water (50 c.c.) for 20 hr., to give tetrafluorosuccinic acid (40%).

Fluorination of 1H : 2H/4H-*Nonafluoro*cyclo*hexane.*—This compound (15·0 g.; b. p. 107°) was introduced from an electrically heated micro-burette into the small static cobaltic fluoride reaction vessel which was at 175—180°. A stream of nitrogen was blown through, and the product (14·0 g.) was washed with water, separated, and dried ($MgSO_4$). Analytical gas chromatography (102°; N_2 flow-rate 1·2 l./hr.) showed the presence of 4 peaks, with retention times the same as those of the compounds mentioned below. Separation (4·43 g.) in the preparative-scale column A gave: (i) undecafluoro*cyclo*hexane (0·03 g.); (ii) a mixture (0·50 g.) of 1*H*/4*H*- and 1*H*/3*H*-decafluoro*cyclo*hexane;[4] (iii) 1*H* : 2*H*/-decafluoro*cyclo*hexane (0·03 g.); and (iv) 1*H* : 2*H*/4*H*-nonafluoro*cyclo*hexane (3·01 g.). The presence of the two compounds in fraction (ii) was shown by gas-phase chromatography on tritolyl phosphate–kieselguhr (1 : 3) (62°; N_2 flow-rate 0·9 l./hr.), and fractions (i)—(iv) had correct infrared spectra.

Fluorination of 1H-*Heptafluoro*cyclo*hexa*-1 : 3-*diene.*—The diene (7·5 g.; b. p. 71·5—72·5°) was introduced into the small static vessel[4] at 55—65° in a nitrogen stream (flow-rate 5 l./hr.).

The products (7·1 g.) were blown from the vessel by nitrogen, and gas-phase chromatography showed the presence of 7 components. Separation (6·13 g.) in the preparative-scale column A (75°; N_2 flow-rate 9·4 l./hr.), gave (i) a mixture (0·11 g.) of dodecafluoro*cyclo*hexane and decafluoro*cyclo*hexene; (ii), undecafluoro*cyclo*hexane (2·27 g.); (iii) a mixed fraction (0·60 g.) containing compounds (ii) and (iv) only; (iv) 1*H*-nonafluoro*cyclo*hex-1-ene (1·80 g.); (v) 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene (0·16 g.); (vi) 4*H*-nonafluoro*cyclo*hex-1-ene [5] (0·08 g.); and (vii) 3*H*-nonafluoro*cyclo*hex-1-ene [5] (0·21 g.). All fractions had correct infrared spectra.

Fluorination of 2H-*Heptafluoro*cyclo*hexa*-1 : 3-*diene*.—The diene (4·2 g.; b. p. 76°), fluorinated as the 1*H*-isomer, yielded a product (6·2 g.) which on analysis by gas chromatography showed the presence of 6 components. Separation as before yielded: (i) dodecafluoro*cyclo*hexane (0·01 g.); (ii) undecafluoro*cyclo*hexane (3·51 g.); (iii) an intermediate fraction (0·69 g.) containing compounds (ii) and (iv) only; (iv) 1*H*-nonafluoro*cyclo*hexene (0·75 g.); (v) 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene (0·03 g.) contaminated with compound (iv); and (vi) a mixture (0·1 g.) of 4*H*- and 3*H*-nonafluoro*cyclo*hexene. These fractions were identified by their infrared spectra.

Preparation of the Four Isomeric 1H : 2H : 4H-*Nonafluoro*cyclo*hexanes* (*with* J. A. GODSELL).—4*H*-Nonafluoro*cyclo*hexene (7·0 g.; b. p. 69°) and an excess of chlorine were sealed together in a " Pyrex " tube which was irradiated with ultraviolet light for 20 hr. The product (7·5 g.) was taken up in ether, washed with sodium metabisulphite solution, then with water, dried ($MgSO_4$), and filtered.

Reduction was carried out in 3 portions. Chlorofluorocarbon (2·5 g.) in ether (30 c.c.) was added slowly to lithium aluminium hydride (0·6 g.) in ether (10 c.c.) at 0° with stirring. After 3½ hr., sulphuric acid was added cautiously, the ethereal layer was separated, and the aqueous layer extracted once with ether. The ether layers and extracts from the three reductions were combined, dried ($MgSO_4$), and filtered. The bulk of the ether was removed by fractional distillation (6″ column packed with 1/16″ × 1/16″ Dixon gauze spirals), and the residue (4·8 g.) was examined by analytical gas chromatography (110°; N_2 flow-rate 1·2 l./hr.), to show the presence of 5 components. The mixture was separated in the preparative-scale column A to give: (i) diethyl ether (2·20 g.); (ii) 1*H* : 4*H*/2*H*-nonafluoro*cyclo*hexane [1] (0·03 g.); (iii) 1*H* : 2*H*/4*H*-nonafluoro*cyclo*hexane (0·46 g.); (iv) 1*H*/2*H* : 4*H*-nonafluoro*cyclo*hexane [1] (0·30 g.); and (v) 1*H* : 2*H* : 4*H*/nonafluoro*cyclo*hexane (0·51 g.) (Found: C, 29·4; H, 1·3%). Compounds (ii)—(v) had correct infrared spectra.

Dehydrofluorination of 1H : 2H : 4H/-*Nonafluoro*cyclo*hexane*.—The compound (13·0 g.; b. p. 124°), potassium hydroxide (50 g.), and water (50 c.c.) were shaken together at 15° for 1¾ hr. The organic layer (8·6 g.) was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography (tritolyl phosphate–kieselguhr 1 : 3; 120°; N_2 flow-rate 1·2 l./hr.) showed the presence of 7 components. Separation of part of the mixture (8·50 g.) in the preparative-scale column A afforded: (i) 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene (1·05 g.); (ii) a mixture (0·63 g.) of compound (i) and 1*H*-heptafluoro*cyclo*hexa-1 : 3-diene; (iii) 2*H*-heptafluoro*cyclo*hexa-1 : 3-diene (0·25 g.); (iv) 1*H* : 5*H*-octafluoro*cyclo*hexene (0·93 g.); (v) 1*H* : 4*H*-octafluoro*cyclo*hexene (1·08 g.), b. p. 86°, n_D^{21} 1·3260 (Found: C, 31·9; H, 0·9%), for which were cited,[13] b. p. 87—88°, n_D^{20} 1·320; (vi) 4*H* : 5*H*/-octafluoro*cyclo*hexene (1·53 g.), b. p. 99°; and (vii) 3*H* : 4*H*/-octafluoro*cyclo*hexene (1·38 g.), b. p. 116°. Fractions (i)—(iv), (vi), and (vii) had infrared spectra identical with those of authentic specimens.

Characterisation of 1H : 4H-*Octafluoro*cyclo*hexene*.—(a) *Oxidation*. The compound (b. p. 86°) yielded 3*H*-heptafluoroadipic acid.

(b) *Dehydrofluorination*. The *cyclo*hexene (7·1 g.), potassium hydroxide (8 g.), and water (10 c.c.) were boiled together for 5 hr. The organic layer (6·4 g.) was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography (100°; N_2 flow-rate 1·1 l./hr.) gave 3 peaks. Separation (5·0 g.) in the preparative-scale column A (85°; N_2 flow-rate 9·4 l./hr.) gave: (i) 1*H*-heptafluoro*cyclo*hexa-1 : 4-diene (2·0 g.); (ii) 1*H*-heptafluoro*cyclo*hexa-1 : 3-diene (1·2 g.); and (iii) 1*H* : 4*H*-octafluoro*cyclo*hexene (1·1 g.). These compounds had correct infrared spectra. The 1*H*-1 : 3-diene was identical with fraction (ii) obtained [1] by dehydrofluorination of 1*H* : 4*H*/2*H*- and 1*H*/2*H* : 4*H*-nonafluoro*cyclo*hexane.

(c) *Fluorination*. The *cyclo*hexene (7·5 g.) on passage through the small static cobaltic fluoride vessel at 45—55° gave a product (8·0 g.) which on analytical gas chromatography showed the presence of 4 components. The first two peaks were identified chromatographically as due to dodeca- and undeca-fluoro*cyclo*hexane. Examination on an alternative packing (silicone oil–silicone rubber 1 : 3; 75°; N_2 flow-rate 0·85 l./hr.) resolved the final peak into two components. Separation of a sample (5·80 g.) in the preparative-scale column A (87°; N_2 flow-rate 9·6 l./hr.) afforded: (i) 1*H*/4*H*-decafluoro*cyclo*hexane (1·01 g.); and (ii) a mixture (3·29 g.) of 1*H* : 4*H*/decafluoro*cyclo*hexane and unchanged 1*H* : 4*H*-octafluoro*cyclo*hex-1-ene. The two components emerging first were not collected. The other two fractions were identified by infrared spectra. Infrared-absorption data indicated that fraction (ii) contained approx. equal quantities of 1*H* : 4*H*/-decafluoro*cyclo*hexane (b. p. 86°), and 1*H* : 4*H*-octafluoro*cyclo*hexene (b. p. 86°), but no other compound.

(d) *Spectroscopy.* The *cyclo*hexene had an infrared –HC=CF– absorption band at 1713 cm.$^{-1}$ but no selective absorption over the range 2400—3000 Å.

Fluorination of 1*H* : 2*H* : 4*H*/*-Nonafluoro*cyclo*hexane.*—This compound (7·5 g.; b. p. 124°) was introduced into the small static reaction vessel at 205°. The products (9·8 g.) were blown from it by a stream of nitrogen, and analytical gas chromatography showed the presence of 6 components. Separation of a sample (8·8 g.) in the preparative-scale column A afforded: (i) dodecafluoro*cyclo*hexane (0·01 g.); (ii) undecafluoro*cyclo*hexane (3·1 g.); (iii) 1*H* : 4*H*/-decafluoro*cyclo*hexane (2·1 g.); (iv) 1*H* : 2*H*/-decafluoro*cyclo*hexane (0·5 g.); (v) 1*H* : 3*H*/-decafluoro*cyclo*hexane (0·7 g.); and (vi) unchanged 1*H* : 2*H* : 4*H*/-nonafluoro*cyclo*hexane, b. p. 124°. These compounds had correct infrared spectra.

Fluorination of Benzene by Manganic Fluoride.—Benzene (100 c.c.) was introduced into a vessel, constructed of nickel and of the type described in a previous paper.[21] It was filled with manganic fluoride (3 kg.) and operated at 200—250°. The fluorination was carried out as described for analogous reactions with cobaltic fluoride. The liquid product (170 g.) was removed from the cold trap after the vessel had been swept out with a stream of nitrogen. It was then washed with water, dried ($MgSO_4$), and filtered. The combined products (800 g.) from several runs were fractionally distilled [4′ column packed with Dixon gauze spirals (1/16″ × 1/16″)]. Only two pure fractions were obtained: (i) 1*H* : 4*H*-octafluoro*cyclo*hexene (180 g.), b. p. 86°; and (ii) 1*H* : 2*H* : 4*H*-heptafluoro*cyclo*hexene (80 g.), b. p. 106°. Fear and Thrower obtained [13] an octafluoro-, b. p. 87° (14·7%), and a heptafluoro-*cyclo*hexene- b. p. 106° (8·8%). By infrared spectroscopy, it was shown that fraction (i) was identical with the material of b. p. 86° obtained by dehydrofluorination of 1*H* : 2*H* : 4*H*/-nonafluoro*cyclo*hexane, and that fraction (ii) was identical with the unsaturated component of the fraction, b. p. 106—107°, isolated from the benzene–cobaltic fluoride reaction.

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