

487. *Fluorocyclohexanes. Part I. cis- and trans-1H : 2H-Decafluorocyclohexanes.*

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Improved conditions are described for the preparation of polyfluorocyclohexanes^{1,2} by the treatment of benzene with cobaltic fluoride at 150–200°. The investigations were considerably simplified by application of gas chromatography. Besides the undeca- and deca-fluorocyclohexanes described before,²⁻⁴ a fraction, b. p. 70°, has been isolated and identified, after dehydrofluorination studies, as *trans-1H : 2H*-decafluorocyclohexane (I). Re-examination of an alternative synthesis of *1H : 2H*-decafluorocyclohexane showed that the product, b. p. 91°, obtained before⁵ was the *cis*-isomer (II), but that a small proportion of the *trans*-compound was formed as well. These allocations of structure have been confirmed by measurements of dipole moments.

EARLIER studies^{1,2} have dealt with the production of polyfluorocyclohexanes by the fluorination of benzene, in the vapour phase, with cobaltic fluoride at about 150°. In this paper we describe improvements in the preparation of these polyfluorides, including the application of gas chromatography^{4,6} to the detection and isolation of the individual compounds. Also, a further component of the mixture, a *1H : 2H*-decafluorocyclohexane (I), has been identified. Since another compound (II) having this basic structure had been reported from an alternative synthesis,⁵ investigations of the stereochemistry of these highly fluorinated cyclohexanes have now been initiated.

Preparation and Isolation of the Polyfluorocyclohexanes.—For the fluorination of benzene a copper reaction vessel, incorporating a stirrer and based on an earlier design,⁷ was used, and gave consistently good yields. As before, for the isolation of pure components, nearly all of which are low-melting solids, fractional distillation was employed. Much trouble had been experienced previously in removing the relatively small proportion of perfluorocyclohexane, which, having no liquid range, sublimed and blocked the fractionating equipment. This was overcome by addition of diethyl ether which forms an azeotrope with perfluorocyclohexane but not with fluorohydrocarbons present. The two chief products

¹ Barbour, Mackenzie, Stacey, and Tatlow, *J. Appl. Chem.*, 1954, **4**, 341.

² *Idem, ibid.*, p. 347.

³ Evans and Tatlow, *J.*, 1954, 3779.

⁴ *Idem, (a) J.*, 1955, 1184; (b) "Vapour Phase Chromatography" (ed. Desty), Butterworths, London, 1956, p. 256.

⁵ Roylance, Tatlow, and Worthington, *J.*, 1954, 4426.

⁶ James and Martin, *Biochem. J.*, 1952, **50**, 679; *Analyst*, 1952, **77**, 915.

⁷ Barbour, Barlow, and Tatlow, *J. Appl. Chem.*, 1952, **2**, 127.

in the lower boiling range, as before, were undeca- and deca-fluorocyclohexane (b. p. 78°), but an inflexion at about 70° in the distillation curves prompted refractionation of intermediates, which gave a new product (I). At this point in the investigation, gas chromatography became available^{6,4} and considerably simplified the separation of the complex polyfluorocyclohexane mixture. Preliminary analytical gas chromatography showed at least ten components (see Table). Fractional distillations of this product (2–3 kg., through 4' columns) were then controlled by analytical chromatography, which improved the efficiency since the purity of fractions was assessed as they were being collected. Most of the major components of the mixture were obtained reasonably pure in this way.^{4b,8}

Characterisation of the 1H : 2H-Decafluorocyclohexanes.—Elemental analysis showed that the new polyfluoride (I) (b. p. 70°) was a decafluorocyclohexane. It was unusually resistant to aqueous potassium hydroxide : under conditions by which undecafluorocyclohexane was converted completely into perfluorocyclohexene, less than half of the new decafluoride had been attacked, as was shown by the liberation of fluoride ion. Analytical gas chromatography of the product showed four peaks, coincident with those given by perfluorocyclohexa-1 : 3-diene³ (III), 1H-nonafluorocyclohex-1-ene⁵ (IV), the starting material (I), and 3H-nonafluorocyclohex-1-ene⁴ (a very small peak only was given by this component). A second treatment with alkali removed the starting material (I) and the trace of 3H-olefin, leaving the 1 : 3-diene (III) and the 1H-ene (IV). The isolation of pure specimens of these olefins (they have very similar properties and almost identical boiling points) could be accomplished only by preparative-scale gas chromatography.⁴ Even with this technique it was necessary to use favourable conditions (low column temperature, small initial charge of the mixture) to effect a clean separation. The diene sample (ca. 16% of the product) was characterised by gas chromatography and infrared spectroscopy. The mono-olefin (IV) (80% of the product) was identified chromatographically, by its infrared spectrum, and by oxidation to octafluoroadipic acid. The very small amount of 3H-nonafluorocyclohex-1-ene present was only detected chromatographically; 4H-nonafluorocyclohex-1-ene⁴ was never detected in these investigations.

The formation by dehydrofluorination of the olefins (III) and (IV) and the complete

Gas chromatography of the polyfluorocyclohexane mixture.

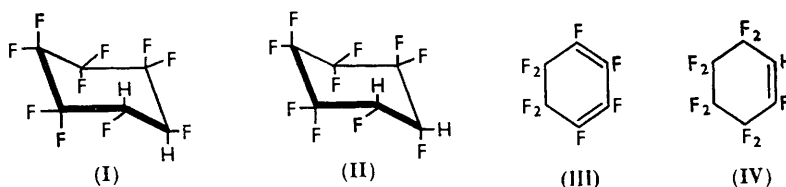
No. of peak	1	2	3	4	5	6
Retention time (min.)	2.2	5.1	6.6	7.5	12.9	16.6
Relative peak area *	m	l	—	m	l	m
Compound	C ₆ H ₁₂	C ₆ H ₈ F ₁₁	Et ₂ O	<i>trans</i> -1H : 2H Mixed †		1H : 4H †
B. p.	—	63°	34°	70°	C ₆ H ₂ F ₁₀ 78°	86°
No. of peak	7	8	9	10	11	12
Retention time (min.)	20.0	25.6	33.4	45.0	50.0	53.0
Relative peak area *	l	s	s	m	s	m
Compound	C ₆ H ₃ F ₉ †	C ₆ H ₂ F ₁₀ †	C ₆ H ₂ F ₁₀ †	Not yet identified		
B. p.	92°	91°	89°	—	—	—

* l = large, m = medium, s = small. † To be reported later.

absence from the products of 4H-nonafluorocyclohex-1-ene clearly established that the new decafluoride (I) (b. p. 70°) possessed a 1H : 2H-structure. However, a different compound (II) (b. p. 91°) having this basic structure had been made earlier,⁵ by an unequivocal synthesis involving the photochemical addition of chlorine to decafluorocyclohexene, and then replacement of the chlorine by hydrogen by means of lithium aluminium hydride. Accordingly, this work⁵ was repeated, and analytical chromatography of the product revealed the presence, not only of the high-boiling form (II) as the major component, but also of the new isomer (I) in smaller amounts, not detected previously. Both compounds were isolated by preparative-scale chromatography, and characterised completely. The

⁸ Godsell, Stacey, and Tatlow, *Nature*, 1956, **178**, 199, and unpublished work.

dehydrofluorination of the two isomers (I) and (II) was repeated. The two samples of the more volatile compound (I), isolated from the polyfluorocyclohexane mixture and from the reduction product of the 1 : 2-dichloride, gave an identical gas-chromatographic trace. This showed the presence of the 1 : 3-diene (III), the 1*H*-mono-ene (IV), and the starting material. In confirmation of the earlier work,⁹ the higher-boiling decafluoride (II), under similar conditions, gave only the 1*H*-ene (IV), with no starting material. A very small step on the leading edge of the peak given when the chromatographic tube was overloaded with this sample of the olefin (IV) may have been due, however, to the presence of a trace of the diene (III).



Stereoisomerism of the 1H : 2H-Decafluorocyclohexanes.—There are two stereoisomers of a 1 : 2-disubstituted cyclohexane,^{9, 10, 11} of which, for convenience, these decafluorocyclohexanes may be considered examples, though of course the two hydrogen “substituents” are smaller than the fluorine atoms. The *cis*-form has one axial and one equatorial hydrogen atom in both possible conformations. These are mirror images of each other, but, presumably, resolution of the optical isomers is impossible. The *trans*-form, in one conformation, has both hydrogen atoms in axial positions, whilst in the other, both are equatorial. In this case, each conformation can exist in mirror-image forms, and resolution of these optical isomers should theoretically be possible, since they are not interconvertible. Experimentally, neither stereoisomer (I) or (II) was optically active; the *trans*-form should of course be synthesised as a racemate. No ready means of resolving fluorohydrocarbon racemates is available at present.

As a mechanism¹² by which dehydrohalogenations of cyclohexane derivatives proceed, the preferred process is generally considered to be a concerted bimolecular one (E_2), in which the eliminated groups, hydrogen and halogen, are originally *trans* to each other, *i.e.*, occupy axial positions. For the all-*cis*-structure “ β -benzene hexachloride,” the slow bimolecular dehydrochlorination is thought^{13, 14} to proceed *via* a carbanion intermediate. Another possible mechanism, the two-stage unimolecular elimination (E_1), has not been established for alkaline dehydrochlorinations. Dehydrohalogenations of 1 : 1- and 1 : 2-dihalogencyclohexanes by aqueous-alcoholic sodium hydroxide have been studied recently.¹⁵ The 1 : 1- and *cis*-1 : 2-dihalides gave exclusively the analogous 1-halogencyclohex-1-ene with elimination of 1 mol. of hydrogen halide by the concerted mechanism (E_2). The *trans*-1 : 2-dihalides eliminated 2 mol. of hydrogen halide to give exclusively cyclohexa-1 : 3-diene in a slow bimolecular reaction (no *cis*-elimination occurred). The influence of conformation is very striking here. Dehydrochlorination¹⁶ of *trans*-1 : 2-dichlorocyclohexane with quinoline, however, gave approximately equimolar amounts of 1-chlorocyclohex-1-ene (*cis*-elimination) and the 1 : 3-diene (*trans*-elimination).

On the assumption that these mechanisms applied also to polyfluorocyclohexanes, the relative ease of dehydrofluorination of the higher-boiling decafluoride (II) suggested

⁹ (a) Hassel, *Quart. Rev.*, 1953, **7**, 221; (b) Barton and Cookson, *ibid.*, 1956, **10**, 44.

¹⁰ Orloff, *Chem. Rev.*, 1954, **54**, 347.

¹¹ Riemschneider and Geschke, *Angew. Chem.*, 1953, 390.

¹² Ingold, “Structure and Mechanism in Organic Chemistry,” Bell, London, 1953, p. 419.

¹³ Cristol, *J. Amer. Chem. Soc.*, 1947, **69**, 338; Cristol, Hause, and Meek, *ibid.*, 1951, **73**, 674.

¹⁴ Orloff and Kolka, *ibid.*, 1954, **76**, 5484.

¹⁵ Goering and Espy, *ibid.*, 1956, **78**, 1454.

¹⁶ Stevens and Grummitt, *ibid.*, 1952, **74**, 4876.

that it was the *cis*-isomer. The possession of one axial and one equatorial hydrogen atom ensured that a hydrogen and a fluorine atom of the $-\text{CHF}\cdot\text{CHF}-$ system were always axial, so that loss of hydrogen fluoride could occur by the orthodox process (E_2) to give the mono-olefin. Since the stability of carbon-fluorine bonds is greater in CF_3 and CF_2 than in CHF groups, the experimental loss of fluorine from position 2 rather than from position 6 is readily understandable.

The lower-boiling decafluoride (I) was much more resistant to dehydrofluorination than its isomer (II), and gave a mixture of the monolefin (IV) and the conjugated diolefin (III). This also is in accord with the expected stereochemical requirements, since the *trans*-isomer, with both hydrogen atoms axial or both equatorial, cannot exist in a form which would allow *trans*-elimination of hydrogen fluoride from the $-\text{CHF}\cdot\text{CHF}-$ system ($\text{C}_{(1)}$ and $\text{C}_{(2)}$). The favoured conformation of the *trans*-isomer should be that with the small hydrogen atoms arranged axially, and then dehydrofluorination could proceed either by a *cis*-elimination of hydrogen fluoride from $\text{C}_{(1)}$ and $\text{C}_{(2)}$ to give the olefin (IV) or by a two-fold *trans*-elimination ($\text{C}_{(1)}$ and $\text{C}_{(6)}$, $\text{C}_{(2)}$ and $\text{C}_{(3)}$) to give the diene (III). The first reaction would be favoured electronically (because of the increased stability of fluorine in CF_2 compared with CHF); the second would be favoured stereochemically. In practice, the electronically favoured *cis*-elimination appears to predominate. *cis*-Eliminations from *trans*-substituted toluene-*p*-sulphonyl esters of cyclohexane derivatives have been reported;¹⁷ the acidity increase of the hydrogen here overshadows the stereochemical effect. Qualitatively, the dehydrofluorination of the *trans*-1*H* : 2*H*-decafluoride (I) is slower than that of undecafluorocyclohexane, though here also the fluorine is lost from a CF_2 group. The greater acidity of a hydrogen atom flanked by two CF_2 groups, compared with one flanked by CF_2 and CHF, may explain this effect.

These allocations of structure were tested by measurements of the dipole moments of the two 1*H* : 2*H*-decafluorides, those of undecafluorocyclohexane and perfluorocyclohexane being measured also for comparison. Results were : C_6F_{12} , 0; C_6HF_{11} , 1.64; $\text{C}_6\text{H}_2\text{F}_{10}$ (b. p. 91°), 2.59; $\text{C}_6\text{H}_2\text{F}_{10}$ (b. p. 70°), 0.88. The value for the isolated C-H dipole in a polyfluoride agrees well with those reported recently for fluoroform¹⁸ (1.62), pentafluoroethane¹⁸ (1.54), and for 1*H*-heptafluoropropane¹⁹ (1.62 ± 0.12). The expected dipole moment of the two equivalent *cis*-structures (1*H* a : 2*H* e and 1*H* e : 2*H* a), calculated from that of the undecafluoride, is 2.69. This is in reasonable agreement, considering the approximations inherent in the determinations, with the experimental value (2.59) found for the isomer of b. p. 91° (II). In the case of the isomer of b. p. 70° (I), the experimental value (0.88) of the dipole moment is sufficiently low to show that this compound must have the *trans*-structure, and that the conformation with the two axial hydrogen atoms predominates. The 1*H* e : 2*H* e conformation of the structure would have a dipole moment very similar (calculated value 2.69) to that of the *cis*-isomer, whereas the 1*H* a : 2*H* a conformation is the only 1*H* : 2*H*-system that should have a very low moment. The experimental value may result (i) from small experimental errors, (ii) from the small dipole inherent in a system with two diaxial hydrogen atoms (the so-called inductive effect), (iii) from the presence of some of the conformation with two equatorial hydrogens, or from a combination of these factors. Because of this uncertainty, it would not seem justifiable to calculate the ratio of the numbers of molecules in each conformation, or the energy difference between the two forms. Suffice it that calculations directly from the experimental dipole moment show that apparently in not more than about 10% of the molecules are the hydrogen atoms equatorial; probably the proportion is less than this.

Thus, all the evidence so far available, both chemical and physical, indicates that the two products obtained are *trans*-(1*H* a : 2*H* a) (I), b. p. 70°, and *cis*-1*H* : 2*H*-decafluorocyclohexane (1*H* a : 2*H* e) (II), b. p. 91°. It is of interest that the latter isomer, which

¹⁷ Bordwell and Kern, *J. Amer. Chem. Soc.*, 1955, **77**, 1141.

¹⁸ Di Giacomo and Smyth, *ibid.*, p. 774.

¹⁹ Rogers and Pruett, *ibid.*, p. 3686.

should be less favoured sterically, is the main product from the synthesis involving photochemical addition of chlorine to perfluorocyclohexene followed by reduction with lithium aluminium hydride. If the latter stage proceeds with retention or inversion of configuration, as seems probable, then a predominantly *cis*-addition of chlorine is indicated (*cis*- as well as *trans*-additions of chlorine to tetrachlorocyclohexenes have been reported²⁰). In the case of perfluorocyclohexene, after the first attack by a chlorine atom, the chlorine substituent (being larger than fluorine) should take up an equatorial position. On the adjacent carbon, if the intermediate radical can rearrange so that the fluorine substituent here becomes essentially equatorial, the *cis*-adduct would be obtained as the final product (cf. a rather similar postulate for intermediate carbonium anions^{9b}).

Though fluorocyclohexanes have been investigated very little as yet, much is now known about the important and related chlorocyclohexane series.^{10, 21} Dipole-moment measurements have been made²² on the 1 : 2-dihalogenocyclohexanes with results which indicate that the favoured conformations of the *trans*-compounds are not as for our decafluorides, owing in part to the different sizes of the substituents. Some of the many dehydrochlorination studies reported have been mentioned above. The great strength of the C-F bond and the relatively small size of the fluorine atom together make the fluorocyclohexanes a unique and interesting group. From the polyfluorocyclohexane mixture obtained from benzene, the other four decafluoro- and two nonafluoro-cyclohexanes have now been isolated and characterised²³ and will be described later.

EXPERIMENTAL

Fluorination Apparatus.—This was based on those described earlier.⁷ The chief differences were as follows: the body was of copper tube (3 ft. 6 in. long; $3\frac{1}{4}$ in. internal diam.; $\frac{3}{16}$ in. wall thickness), and the two bearings of the stirrer shaft were simplified. Each comprised a plain bearing (carrying the shaft) adjacent to which was a "Fluon" bush in which the shaft ran. These bushes were compressed into their housings by strong springs, and made efficient self-lubricating gas-tight seals with which no nitrogen-sweep or water-cooling was necessary if the reaction-vessel temperatures did not exceed about 250°. The vessel was charged as before with 3.5 kg. of cobaltic fluoride. The seven heaters were of an improved design, the elements being carried in firebricks (HT 1 Refractory) hollowed out to fit around the tube, and into which slots had been cut. The other features and the ancillary equipment were as described earlier.

Production of Polyfluorocyclohexanes from Benzene.—*Fluorination.* Benzene (65.5 g.) was introduced into the reaction vessel at a steady rate from a dropper during 3 hr. The vessel temperature was initially approx. 170°, along its length, and as the reaction proceeded the heat of reaction gave rise to an increase of 30—50° which passed along the reaction vessel as a narrow "hot zone." No attempt was made to compensate for this increase (somewhat improved yields would have resulted, but at the expense of constant attention: the conditions described required little attention). The apparatus was then swept out with a slow stream of nitrogen for ca. $\frac{1}{2}$ hr. and the trap was warmed to about 20° and the contents were poured into water. The semi-solid product was washed with water until free from hydrogen fluoride, most of the water was decanted, the product was allowed to solidify (cooled below 15°), and the rest of the water was then poured off. The polyfluoride mixture (180 g.) was a white wax, virtually free from benzene (which forms azeotropes with the lower-boiling fluorides).

The cobaltic fluoride in the reaction vessel was regenerated by passage at about 170° of fluorine (ca. 250 g.) during 15 hr. After being swept out with nitrogen the vessel was ready for further use.

Distillation. To the product (1629 g.) from nine such runs, ether (150 c.c.) was added, and

²⁰ Kolka, Orloff, and Griffing, *J. Amer. Chem. Soc.*, 1954, **76**, 3940.

²¹ Metcalf, "Organic Insecticides," Interscience Publ. Inc., New York, 1955, p. 213.

²² Tulinskie, Di Giacomo, and Smyth, *J. Amer. Chem. Soc.*, 1953, **75**, 3552; Kozima, Sakashita, and Maeda, *ibid.*, 1954, **76**, 1965; Bender, Flowers, and Goering, *ibid.*, 1955, **77**, 3463; Kwestroo, Meijer, and Havinga, *Rec. Trav. chim.*, 1954, **78**, 717.

²³ Evans, Godsell, Stephens, and Tatlow, unpublished work.

the solution was washed with aqueous sodium carbonate, then with water, separated, and fractionally distilled, from phosphoric oxide, through a 2' column packed with gauze spirals. Fractions obtained were : the azeotrope of ether and perfluorocyclohexane, b. p. 27.5°; a small excess of ether, b. p. 34° (when the temperature rose above 27.5°, more ether was added until it no longer fell to 27.5°; an excess of ether was then present); undecafluorocyclohexane (345 g.), b. p. 63—64°; intermediate fraction (110 g.), b. p. 64—77° (an inflexion occurred at 70° in the distillation curve); decafluorocyclohexane (185 g.), b. p. 77.5—79°; still residue (700 g.) (solid when cold).

Refluorination. To still residues, b. p. > 80°, similar to that mentioned above (3500 g.), benzene (305 g.) was added, to give a liquid mixture. This was fluorinated, as described before, in 11 batches, at reaction temperatures of about 190°, there being very little heat of reaction. After isolation as described before, the product (2600 g.) was mixed with a little ether and fractionated. After removal of the azeotrope, undecafluorocyclohexane (670 g.), b. p. 63.4—63.7°, and decafluorocyclohexane (250 g.), b. p. 78—79°, were obtained with no evidence of a flat part in the distillation curve corresponding to the compound, b. p. 70°.

Application of gas chromatography. The crude polyfluorocyclohexane mixture was liquefied with a little ether, the mixture (0.01 c.c.) was put through a 6' chromatography column, packed with dinonyl phthalate-kieselguhr (1 : 2), at 100° (nitrogen flow rate 0.45 l./hr.) with the result shown in the Table. The peak given by compound (8) is coincident with that from authentic *cis*-1H : 2H-decafluorocyclohexane, and the boiling point also is identical. The later peaks may well be incompletely resolved. Some material was retained even longer than 60 min., but gave only broad ill-defined peaks under these conditions.

Isolation of the Polyfluoride having b. p. 70°.—Intermediate fractions (590 g.), b. p. 64—77°, from various series of fluorinations, were fractionally distilled through a 2' column. There was obtained, after the removal of undecafluorocyclohexane, *trans*-1H : 2H-decafluorocyclohexane (150 g.), b. p. 70.0—71.0°, m. p. 20.5—21.5°, n_D^{25} 1.2929 (Found : C, 27.1; H, 0.8; F, 71.6. $C_6H_2F_{10}$ requires C, 27.3; H, 0.8; F, 71.9%).

Subsequently, gas chromatography of this product (dinonyl phthalate-kieselguhr 1 : 2, temp. 78°, nitrogen flow rate 1.2 l./hr.) showed, by overloading of the tube, the presence of traces of undecafluorocyclohexane and of decafluorocyclohexane (b. p. 78°). For the later stages of the examination detailed below, the material was purified by passage through the preparative-scale gas-chromatographic column.⁴

Dehydrofluorination of trans-1H : 2H-Decafluorocyclohexane.—*Analytical-scale work.* *trans*-1H : 2H-Decafluorocyclohexane (2.64 g.) was refluxed for 6 hr. with potassium hydroxide (10 g.) and water (10 c.c.) in a flask with a condenser cooled by solid carbon dioxide-alcohol. Titration of the aqueous phase showed that it contained fluoride ion (0.4 mol.). Analytical gas chromatography of the organic phase (A) (dinonyl phthalate-kieselguhr 1 : 2, temp. 55°, nitrogen flow rate 1.0 l./hr.) gave peaks corresponding to perfluorocyclohexa-1 : 3-diene (after 9.5 min.), 1H-nonafluorocyclohex-1-ene (11.0 min.), and much unchanged decafluoride (15.0 min.). A small peak (after 22.0 min.) corresponded with that given by 3H-nonafluorocyclohex-1-ene.

Under identical conditions, undecafluorocyclohexane was completely dehydrofluorinated, fluoride ion (1.08 mol.) was found in the aqueous phase, and the organic product was shown by gas chromatography to be pure perfluorocyclohexene, no undecafluorocyclohexane being detected.

The organic phase (A) described above was re-treated with alkali under identical conditions. Fluoride ion (1.27 mol.) was found in the aqueous phase, and the starting material and 3H-nonafluorocyclohex-1-ene were no longer present in the product, which consisted of the 1 : 3-diene and the 1H-monoene.

It was shown by gas chromatography that 4H-nonafluorocyclohex-1-ene was not present in the dehydrofluorination product at any stage.

Preparative-scale work. The fluorohydrocarbon (10 g.), potassium hydroxide (10 g.), and water (10 c.c.) were shaken in a sealed tube at 100° for 3 hr. Analytical gas chromatography of the product (dinonyl phthalate-kieselguhr 1 : 2, temp. 55°, nitrogen flow rate 1.0 l./hr.) showed the presence of two components only, with peaks (after 9.5 and 11.0 min.) coincident with those given by perfluorocyclohexa-1 : 3-diene and 1H-nonafluorocyclohex-1-ene, respectively. Separation of the product (1 c.c. portions) was carried out in the preparative-scale column⁴ (temp. 30°, nitrogen flow rate 9 l./hr.), the fractions appearing after 5 hr. and 5½ hr. The first (16%) (Found : F, 68.7. Calc. for C_6F_8 : F, 67.8%) gave a single peak (after 9.5 min.) in analytical gas chromatography. It had two infrared bands, at 1710 and 1750 cm^{-1} . The

patterns obtained from both techniques were identical with those given under the same conditions by an authentic specimen³ of octafluorocyclohexa-1:3-diene.

The second fraction (80%) (Found: F, 69.8. Calc. for C_6HF_8 : F, 70.1%) gave a single peak (after 11.0 min.) from analytical gas chromatography. Infrared examination showed a single band at 1710 cm^{-1} (value quoted earlier⁵ for 1H-nonafluorocyclohex-1-ene, 1707 cm^{-1}).

Oxidation of 1H-Nonafluorocyclohex-1-ene.—The olefin (1.8 g.), potassium permanganate (12 g.), sodium hydrogen carbonate (6 g.), and water (30 c.c.) were heated at $120\text{--}130^\circ$ for 15 hr. in a rocking autoclave. Isolation as usual gave crude dianilinium perfluoroadipate (3.0 g.), m. p. $209\text{--}211^\circ$. When recrystallised from acetone-chloroform it had m. p. $210\text{--}211^\circ$ (recovery 86%) (Found: C, 45.1; H, 3.5; F, 31.6. Calc. for $C_{18}H_{16}O_4N_2F_8$: C, 45.4; H, 3.4; F, 31.9%). The m. p. obtained previously² was $210\text{--}212^\circ$.

Preparation of 1H:2H-Decafluorocyclohexanes from Perfluorocyclohexene.—Chlorine was added to the olefin under ultraviolet irradiation.⁵ 1:2-Dichlorodecafluorocyclohexane (25.0 g.) in ether (10 c.c.) was added to lithium aluminium hydride (5 g.) in ether (50 c.c.) which was stirred mechanically at 0° . After $1\frac{1}{2}$ hr., water was added cautiously, followed by 50% sulphuric acid until no precipitate remained. The organic layer was separated, washed, dried, ($MgSO_4$), and distilled (1' column) to remove ether. The residue was distilled from the flask (18.0 g.), and examination by analytical gas chromatography (dinonyl phthalate-kieselguhr 1:2) showed the presence of three components, a little ether, *trans*-1H:2H-decafluorocyclohexane, and the *cis*-analogue. Separation in the preparative-scale gas chromatography column (5 portions, temp. 80° , nitrogen flow rate 9 l./hr.) afforded the *trans*-isomer (4.5 g.), b. p. 70° , m. p. $22\text{--}23^\circ$ (Found: C, 27.3; H, 0.7; F, 71.5%), and the *cis*-isomer (11.4 g.), b. p. 91° (Found: F, 71.8%). In analytical gas chromatography, each of these fractions gave a single peak, coincident with those given by, respectively, the fraction from the fluorination product of benzene described earlier, and the sample, made from perfluorocyclohexene, reported previously.⁵

The *trans*-compound (0.36 g.), made as described above, and 9N-aqueous potassium hydroxide (0.72 c.c.) were shaken in a sealed tube at 100° for $1\frac{1}{2}$ hr. Analytical gas chromatography of the product showed the presence of three components, perfluorocyclohexa-1:3-diene, 1H-nonafluorocyclohex-1-ene, and starting material. The same pattern was given by the sample isolated from the fluorination product of benzene when treated under identical conditions.

The *cis*-isomer, treated likewise, gave, on analytical chromatography, a single peak due to 1H-nonafluorocyclohex-1-ene with no starting material left. A very minor step at the start of the peak may have been due to perfluorocyclohexa-1:3-diene, but if present its concentration was below 1%.

Dipole Moments.—These were determined by the standard method from measurements of the dielectric constants of a number of dilute solutions of the compounds in benzene, with correction terms from the refractive indices of the solutions. Dielectric constants were measured by the "Resonance" method in an apparatus similar to that of Bender;²⁴ the refractive indices were measured by means of a Pulfrich critical-angle refractometer. The results were calculated by Guggenheim's method.²⁵ Measurements were made on perfluorocyclohexane as well as on the three fluorohydrocarbons, but in the former case only very dilute solutions in benzene could be made up (< 3% by wt.). Measurements on the undecafluoride were made with 4 solutions (concentrations, 4–12% by wt.); for the *cis*-decafluoride 4 solutions (2–6% by wt.); and for the *trans*-decafluoride 5 solutions (1.4–7% by wt.), were used. Measurements on chlorobenzene under similar conditions gave the expected value. Though no great accuracy can be claimed, the results enabled a clear distinction to be made between the *cis*- and the *trans*-form.

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²⁴ Bender, *J. Chem. Educ.*, 1946, **23**, 179.

²⁵ Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714; 1951, **47**, 573.