Tetrahedron, 1958, Vol. 2, pp. 193–202. Pergamon Press Ltd., London

FLUOROC*YCLO*HEXANES—III*

1H:4H/2H- AND 1H/2H:4H-NONAFLUOROC*YCLO*HEXANE† AND DERIVED COMPOUNDS

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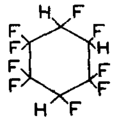
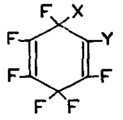
Abstract—Two nonafluoro*cyclo*hexanes of b.p. 92° and 101°, made by fluorination of benzene,[1] have each been dehydrofluorinated to give the same six unsaturated products. These were identified by oxidation and other studies as 3H:4H- and 4H:5H-octafluoro*cyclo*hexene, 1H-1:4-, 1H-1:3-, and 2H-1:3-heptafluoro*cyclo*hexadiene, and hexafluorobenzene,[2] thus indicating a 1H:2H:4H-structure for the saturated precursors. The stereochemistry of the adjacent >CHF groups was established by resolution, via the brucine salt, of the 3H:4H-hexafluoroadipic acid obtained by oxidation of the 4H:5H-mono-olefin, showing that the hydrogens were *trans*. The complete stereochemistry of the nonafluorides was suggested by the dehydrofluorinations and confirmed by further fluorination[3] to give known decafluoro*cyclo*hexanes. Treatment of 4H/5H-octafluoro*cyclo*hexene with lithium aluminium hydride in diethyl ether gave 1H,4H/5H-heptafluoro*cyclo*hexene, a precursor of pentafluorobenzene.[4]

ISOLATION AND DEHYDROFLUORINATION OF THE NONAFLUOROC*YCLO*HEXANES

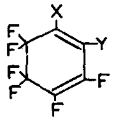
FROM the polyfluoro*cyclo*hexane mixture[1] made from benzene, two new fluorohydrocarbons (b.p. 92°, m.p. 45°, and b.p. 101°, m.p. 12–14°) have been isolated by fractional distillation controlled by analytical gas chromatography.[5] Each was a nonafluoro*cyclo*hexane, and when dehydrofluorinated exhaustively with aqueous potassium



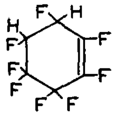
I 1$\underline{\text{H}}$a : 4$\underline{\text{H}}$e/2$\underline{\text{H}}$a
II 1$\underline{\text{H}}$a/2$\underline{\text{H}}$a : 4$\underline{\text{H}}$a



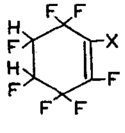
III X=F, Y=H
VII X=H, Y=F



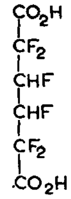
IV X=H, Y=F
V X=F, Y=H



VI 3$\underline{\text{H}}$/4$\underline{\text{H}}$



VIII X=F
X X=H
both 4$\underline{\text{H}}$/5$\underline{\text{H}}$



$HO_2C-CF_2-CHF-CHF-CF_2-CO_2H$

IX

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* Part II, preceding paper.

† The nomenclature used for these *cyclo*hexane derivatives follows that of the inositols (see S. J. Angyal and C. G. Macdonald *J. Chem. Soc.* 686 (1952); D. H. Whiffen *Chem. & Ind.* (*Rev.*) 964 (1956).

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

[2] J. A. Godsell, M. Stacey, and J. C. Tatlow *Nature, Lond.* **178**, 199 (1956).

[3] D. E. M. Evans, J. A. Godsell, R. Stephens, J. C. Tatlow and E. H. Wiseman *Tetrahedron* **2**, 183 (1958).

[4] R. Stephens and J. C. Tatlow *Chem. & Ind.* (*Rev.*) 821 (1957).

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

hydroxide, a relatively difficult reaction in both cases, each gave a mixture (boiling range 66–90°), which was shown by analytical gas chromatography to contain six compounds. Preparative-scale gas chromatography[5] effected the separation of these two mixtures into their components, and it was demonstrated by infra-red spectroscopy,[6,7] and by the identity of the gas chromatographic retention times, that the six products from one nonafluoride were individually the same as those from the other.

CHARACTERISATION OF THE DEHYDROFLUORINATION PRODUCTS

The six compounds formed in the dehydrofluorinations were characterised by oxidative degradation and other studies. The first substance isolated (b.p. 66–67°) analysed as a heptafluoro*cyclo*hexadiene, and was oxidised by aqueous potassium permanganate to give difluoromalonic acid. It showed two bands in the infra-red[7] corresponding to a —CF=CF— and a —CF=CH— double bond, but no strong selective absorption in the ultra-violet (such absorption would have been given by a conjugated diene). These facts showed clearly that the compound was 1H-heptafluoro*cyclo*hexa-1:4-diene (III).

The second and third fractions obtained (b.p. 72° and 76°, respectively) were also heptafluoro-dienes. Each was oxidised to tetrafluorosuccinic acid, and each gave a tetrachloro-addition product with chlorine. Spectroscopically, each gave a strong selective absorption band in the ultra-violet, showing the presence of a conjugated system, and two C=C bands in the infra-red.[7] Thus, these two compounds were 1H- and 2H-heptafluoro*cyclo*hexa-1:3-diene (IV and V), but as yet it has not been possible to decide which compound possesses which structure. Attempts to saturate selectively one of the double bonds of the conjugated system of each compound by reaction with cobaltic fluoride under very mild conditions, which might have given a different range of nonafluoro*cyclo*hexenes in the two cases, were not successful. It is of interest that these conjugated dienes exhibited similar instability when exposed to the atmosphere to that shown [8] by perfluoro*cyclo*hexa-1:3-diene.

The fourth product isolated from the original dehydrofluorination had b.p. 80° and was hexafluorobenzene; its characterisation has been described already.[2]

The fifth compound had b.p. 85° and was an octafluoro*cyclo*hexene. Addition of chlorine gave a dichloro-octafluoro*cyclo*hexane, and the presence of a —CF=CF— group was indicated by infra-red analysis.[7] Oxidation afforded a hexafluoroadipic acid, proving that no hydrogen was carried directly on the double bond. When the acid was treated with alkaline potassium permanganate, tetrafluorosuccinic acid was produced. The hexafluoroadipic acid was very susceptible to attack by bases, attempts to prepare an anilinium salt and an amide failing. This behaviour is typical[3,9] of acids with α-carbons carrying hydrogen and β-carbons carrying fluorine substitutents. All this evidence shows that the acid was 2H:3H-hexafluoroadipic acid, and, from the work on the stereochemistry of the —CHF—CHF— system in all these compounds (see later), it can be given the DL-*threo*-configuration. The original olefin was thus 3H:4H-octafluoro*cyclo*hex-1-ene (VI). Confirmation of this structure was obtained by dehydrofluorination, which afforded 3 products, identified by gas

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[6] D. Steele and D. H. Whiffen. In press.

[7] J. Burdon and D. H. Whiffen. *Tetrahedron* (to be submitted shortly).

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

[9] M. W. Buxton, M. Stacey and J. C. Tatlow *J. Chem. Soc.* 366 (1954).

chromatography and infra-red spectroscopy as the two conjugated dienes (IV and V) and hexafluorobenzene. The last compound presumably must have been formed by a 1:4-elimination process from 3H-heptafluoro*cyclo*hexa-1:4-diene (VII), though this intermediate was not found in the product formed under the reaction conditions employed. Neither hexafluorobenzene nor the 4H:5H-olefin (VIII), which gives it by a 1:2-elimination, could be detected in the sample of the starting material (VI) used.

The sixth product (b.p. 90°) of the reaction of the nonafluorides (I and II) with alkali was another octafluoro*cyclo*hexene which gave a dichloro-addition product, and had an infra-red spectrum[7] suggesting the presence of a CF=CF group. This was confirmed by the production of a new hexafluoroadipic acid upon oxidation. Degradation of this C_6-acid with alkaline permanganate afforded difluoromalonic acid. This established the structure of the former as 3H:4H-hexafluoroadipic acid (IX), and thence of the original olefin as 4H:5H-octafluoro*cyclo*hex-1-ene (VIII). The latter structure was confirmed by dehydrofluorination, which proceeded only slowly but afforded two products, the 1H-1:4-diene (III) and hexafluorobenzene.

STRUCTURES OF THE NONAFLUORO*CYCLO*HEXANES

The dehydrofluorination products obtained from the nonafluoro*cyclo*hexanes (I) and (II) showed clearly that the latter must be 1H:2H:4H-compounds. By orthodox elimination processes, 1H:2H:3H-nonafluorides could not give the 4H:5H-olefin (VIII) or the unconjugated diene (III), whilst 1H:3H:5H-nonafluorides could give only hexafluorobenzene of the products found. The pattern of unsaturated derivatives obtained also indicated that, with both nonafluorides, the isolated hydrogen on position 4 was the initial point of attack. By analogy with the results obtained earlier[1] for the 1H:2H-decafluoro*cyclo*hexanes, this suggested that the hydrogens on carbon atoms 1 and 2 were *trans*, and hence that, being smaller than fluorine, they occupied *axial* positions. An unequivocal method for establishing the stereochemistry of this part of the molecule was available, however. The configuration of the asymmetric carbon atoms (3 and 4) of the 3H:4H-hexafluoroadipic acid (IX), obtained by oxidation of the olefin (VIII), was clearly the same as that of carbon atoms 1 and 2 of both of the parent nonafluoro*cyclo*hexanes. If this arrangement was *trans*, i.e. if each of the hydrogens was *axial*, the hexafluoroadipic acid must be a DL-mixture which would be resolvable. If one hydrogen was *axial* and one *equatorial*, the derived acid would be an optically inactive *meso*-form. By the classical method of resolution, fractional crystallisation of the brucine salts, the 3H:4H-hexafluoroadipic acid (IX) was resolved successfully into its *dextro*- and *laevo*-enantiomorphs. This proved conclusively that both of the nonafluoro*cyclo*hexanes (I and II) were *trans* (1Ha/2Ha)-isomers. Obviously, the mono-olefins (VI and VIII) also had the *trans*-structure, and were, respectively, 3H/4H-, and 4H/5H-octafluoro*cyclo*hex-1-ene. A qualitative comparison of the rates of dehydrofluorination of the nonafluorides (I and II) indicated that the isomer (II) (b.p. 101°) reacted more readily under mild conditions to give the two mono-olefins (VI and VIII) than did the isomer (I). It was assumed therefore that the former (II) had a 4Ha-structure, and the latter (I) a 4He-structure.

Confirmation of these configurations was provided by further fluorination of the nonafluorides (I and II) using cobaltic fluoride. The experimental details of these reactions are described in the previous paper[3]. The isomer (I) gave 3 decafluoro*cyclo*hexanes which have been shown by independent studies[3] to possess the 1Ha/2Ha (b.p. 70°), the 1Ha/3He (b.p. 78°) and the 1Ha:4He/ (b.p. 86°) structures. The isomer (II) likewise gave the known[3] 1Ha/2Ha, 1Ha:3Ha/ (b.p. 89°), and 1Ha/4Ha (b.p. 78°) decafluorides. Hence, the two parent compounds investigated in this paper are 1Ha:4He/2Ha- (I) and 1Ha/2Ha:4Ha-nonafluoro*cyclo*hexane (II). The two independent studies of the decafluoride and the nonafluoride series have thus been related completely, the structural assignments in each being supported by those in the other. Further evidence confirming the stereochemical allocations has also been obtained from the infra-red studies.[6]

The isolation of the mono-olefin (VIII) enabled a synthesis to be effected of the then unkown aromatic compound pentafluorobenzene. Earlier work[10] in this department has shown that ethereal lithium aluminium hydride reacts readily with fluoro-olefins, with progressive replacement of vinylic fluorines by hydrogen, probably by an addition-elimination mechanism. 4H/5H-Octafluoro*cyclo*hexene (VIII) reacted with the metal hydride in this way to give 1H, 4H/5H-heptafluoro*cyclo*hex-1-ene (X), together with two new hexafluoro*cyclo*hexenes that were not investigated. The structure of the heptafluoride (X) was confirmed by its infra-red spectrum[7] (a band at 1710 cm^{-1} indicated a CF=CH group) and by oxidation to give the same hexafluoroadipic acid (IX) as had been formed from the parent octafluoride (VIII). Dehydrofluorination of the heptafluoride (X) afforded the desired pentafluorobenzene. However, an easier synthesis of this new fluoro-aromatic compound had by then been developed,[4] starting from a major component of the polyfluoro*cyclo*hexane mixture, a 1H:2H:4H:5H-octafluoro*cyclo*hexane.

Interesting new fields of study are opened up by these syntheses of aromatic polyfluoro-compounds from members of the fluoro*cyclo*hexane series.

EXPERIMENTAL

1H:4H/2H- *and* 1H/2H:4H-*nonafluoro*cyclo*hexane*

Fractional distillation controlled by analytical gas chromatography[5] of the partly fluorinated *cyclo*hexane mixture[1,3] having b.p. > 91·7° gave[2] 1H:4H/2H- (b.p. 92·0–92·5°, m.p. 44–46°), a mixed intermediate fraction, and 1H/2H:4H-*nonafluoro*-cyclo*hexane*, b.p. 101°, m.p. 12–14°, n_D^{14} 1·3194 (Found: C, 29·4; H, 1·2. Calc. for $C_6H_3F_9$: C, 29·3; H, 1·2%). These nonafluorides were obtained in yields of, respectively, ca. 10 per cent and ca. 5 per cent of the original polyfluoride mixture. These yields may be increased by using lower fluorination temperatures.

The 1H:4H/2H-isomer gave peak no. 7 in the table of gas chromatography results given earlier.[1] The other isomer was peak no. 12, but under the conditions used resolution is inferior for the compounds of long retention times.

Dehydrofluorination of 1H:4H/2H-*nonafluoro*cyclo*hexane*

The polyfluoride (11·0 g, b.p. 92°), potassium hydroxide (10·0 g) and water (10 cc) were heated together under reflux for 6 hr (two condensers in series were used, one cooled by water and one by solid carbon dioxide). The organic phase (9·0 g) was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography (dinonyl phthalate/kieselguhr 1 : 2, temp. 82°, N_2 flow rate 1·6 l/hr) showed 6 peaks with retention times (in minutes) of 9·1 (*w*), 11·3 (*m*), 15·7 (*w*), 25·5 (*w*), 28·5 (*vs*), and 33·5 (*s*), respectively. Separation of the mixture in the preparative-scale gas

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[10] D. E. M. Evans and J. C. Tatlow Unpublished results.

chromatography column[5] (16 ft long × 3 cm dia., dinonyl phthalate/kieselguhr 1 : 2, temp. 80°, N_2 flow rate 10 l/hr), followed by distillation of each fraction *in vacuo*, afforded respectively: (i) 1H-*heptafluoro*cyclo*hexa*-1:4-*diene* (0·18 g), b.p. 66·5–67·0°, n_D^{18} 1·3275 (Found: C, 35·1; H, 0·6. Calc. for C_6HF_7: C, 35·0; H, 0·5%); (ii) *heptafluoro*cyclo*hexa*-1:3-*diene* (1·37 g), b.p. 71·5–72·5°, n_D^{18} 1·3400 (Found: C, 34·7; H, 0·4%); (iii) *heptafluoro*cyclo*hexa*-1:3-*diene* (0·51 g), b.p. 76°, n_D^{18} 1·3383 (Found: C, 35·1; H, 0·7%); (iv) hexafluorobenzene (0·46 g), b.p. 80°, n_D^{18} 1·3746 (Found: C, 38·6; F, 62·0. Calc. for C_6F_6: C, 38·7; F, 61·3%); (v) 3H/4H-*octafluoro*cyclo*hex*-1-*ene* (3·75 g), b.p. 85°, n_D^{18} 1·3277 (Found: C, 31·6; H, 0·9; F, 66·9. Calc. for $C_6H_2F_8$: C, 31·9; H, 0·9; F, 67·2%); and (vi) 4H/5H-*octafluoro*cyclo*hex*-1-*ene* (2·51 g), b.p. 90°, n_D^{18} 1·3283 (Found: C, 32·2; H, 1·2%).

The relative proportions of the products were varied by alteration of the reaction conditions, more drastic treatment increased the amounts of products (i)–(iv) at the expense of (v) and (vi), particularly of (v), which was dehydrofluorinated more readily than (vi).

The conjugated dienes (ii) and (iii) were unstable, and after a few days samples became turbid and hydrogen fluoride was present (cf. octafluoro*cyclo*hexa-1:3-diene[8]). This decomposition was retarded by storage in well-stoppered vessels at 0°.

In the early stages of the work[5] it was thought that nine products were formed in this dehydrofluorination. However, three of these gave only very small peaks with low retention times in gas chromatography. They were identified later as perfluoro*cyclo*-hexa-1:3- and -1:4-diene, and 1H-nonafluoro*cyclo*hexene, and arose[3] from traces of 1H:3H/- (b.p. 89°), and 1H:2H/- decafluoro*cyclo*hexane (b.p. 91°), respectively, in the nonafluoride samples. These impurities are removed by careful fractional distillation as described above.

Characterisation of 1H-*heptafluoro*cyclo*hexa*-1:4-*diene*

(a) *Oxidation*. The diene (1·12 g), potassium permanganate (10 g), and water (50 cc) were shaken in an autoclave at 20° for 14 hr and the temperature was then raised to 100° for 4 hr. Isolation as usual [8,11] gave dianilinium difluoromalonate (42 per cent), m.p. 161–162° (from acetone–chloroform) (Found: C, 55·0; H, 4·8%; equiv., 164. Calc. for $C_{15}H_{16}O_4N_2F_2$: C, 55·2; H, 4·9%; equiv., 163) and di-(*S*-benzylthiuronium) difluoromalonate, m.p. 184–185° (Found: C, 48·2; H, 4·8. Calc. for $C_{19}H_{22}O_4N_4S_2F_2$: C, 48·3; H, 4·7%). Cited[8] melting points were 160–161° and 180–182°, respectively.

(b) *Spectroscopy*. The diene showed two bands in the infra-red at 1723 and 1770 cm^{-1}. No selective absorption was shown in the ultra-violet over the range 2400–3000 Å.

*Characterisation of the heptafluoro*cyclo*hexa*-1:3-*diene of b.p.* 72°

(a) *Oxidation*. Treatment as usual at 100° for 17 hr with aqueous permanganate afforded, by the standard isolation process,[8] dianilinium tetrafluorosuccinate (20 per cent), m.p. 224–225° (Found: C, 51·2; H, 4·4%; equiv., 187. Calc. for $C_{16}H_{16}O_4N_2F_4$: C, 51·1; H, 4·3%; equiv., 188). The di-(*S*-benzylthiuronium) salt had m.p. 189–190° (Found: C, 45·8; H, 4·4. Calc. for $C_{20}H_{22}O_4N_4S_2F_4$: C, 46·O; H, 4·2%). Cited[8] melting points were 224–225°, and 189–190°, respectively.

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

(b) *Addition of chlorine.* The 1:3-diene (2·0 g, b.p. 72°) and chlorine (1·5 g) were sealed in a hard-glass tube which was irradiated with ultra-violet light for 18 hr. The mixture was poured into aqueous sodium metabisulphite, separated, dried (P_2O_5), and distilled to give 1:2:3:4-*tetrachloroheptafluoro*cyclo*hexane* (2·63 g), b.p. 197–199°, m.p. 55° (Found: C, 20·8; H, 0·4. Calc. for $C_6HCl_4F_7$: C, 20·7; H, 0·3%).

(c) *Spectroscopy.* Two bands were shown in the infra-red, at 1682 and 1743 cm^{-1}. In the ultra-violet there was a band at (max.) λ2540 Å, ε (approx.) 3720 (*c*, 0·027 g/l. in ethanol).

*Characterisation of the heptafluoro*cyclo*hexa*-1:3-*diene of b.p.* 76°

(a) *Oxidation.* This afforded tetrafluorosuccinic acid, as the dianilinium salt (49 per cent), m.p. 224–225° (Found: C, 50·8; H, 4·1%; equiv., 189), and the di-(*S*-benzylthiuronium) salt m.p. 186–187° (Found: C, 45·8; H, 4·0%).

(b) *Addition of chlorine.* Carried out as before, this gave, as a colourless liquid, a 1:2:3:4-*tetrachloroheptafluoro*cyclo*hexane* (74 per cent), b.p. 184–185° (Found: C, 20·1; H, 0·3%).

(c) *Spectroscopy.* Two bands were shown in the infra-red, at 1679 and 1732 cm^{-1}, and one in the ultra-violet at (max.) λ2625 Å, ε (approx.) 3070 (*c*, 0·086 g/l. in ethanol).

Characterisation of 3H/4H-*octafluoro*cyclo*hex*-1-*ene*

(a) *Oxidation.* The olefin (1·8 g), potassium permanganate (15 g), sodium bicarbonate (3 g), and water (50 cc) were heated at 85° for 16 hr in a rocking autoclave. Treatment as usual gave an acidic solid (1·67 g). Distillation of part (0·22 g) of this at 160–170° (bath temp.)/15 mm onto a cold finger gave the hygroscopic DL-threo-2H:3H-*hexafluoroadipic acid* (0·18 g), m.p. 126–128° (Found: C, 28·1; H, 1·8%; equiv., 125. Calc. for $C_6H_4O_4F_6$: C, 28·4; H, 1·6%; equiv., 127). The crude acid (0·29 g) in water (pH 4) was treated with aqueous *S*-benzylthiuronium chloride to give the *di-*(S-*benzylthiuronium*) salt (0·11 g) (from water), m.p. 226–227° (Found: C, 45·0; H, 4·2; F, 19·6. Calc. for $C_{22}H_{24}O_4N_4S_2F_6$: C, 45·0; H, 4·1; F, 19·4%).

This acid and its derivatives were not very stable, and attempts to prepare a dianilinium salt and a diamide failed. In the former case, a sticky solid was obtained: in the latter, fluoride ion was eliminated, and a product of wide melting-range formed.

(b) *Addition of chlorine.* The olefin (1·97 g), treated as before, gave, as a colourless liquid, 1H:2H-3:4-*dichloro-octafluoro*cyclo*hexane* (1·81 g), b.p. 143–144° (Found: C, 23·4; H, 0·5. Calc. for $C_6H_2Cl_2F_8$: C, 24·3; H, 0·7%).

(c) *Dehydrofluorination.* The olefin (2·23 g, no impurities were detectable in analytical gas chromatography), potassium hydroxide (10 g) and water (10 cc) were boiled together for 8 hr. After being washed with water and dried ($MgSO_4$), the product (1·34 g) showed 3 peaks in analytical gas chromatography (conditions as before), with retention times the same as those of authentic samples of the two conjugated dienes and hexafluorobenzene. Separation (1·19 g) in the preparative-scale column gave heptafluoro*cyclo*hexa-1:3-diene (0·72 g), b.p. 72°; the position isomer (0·26 g) b.p. 76°; and hexafluorobenzene (0·14 g), b.p. 80°. These three compounds had infra-red spectra identical over the range 650–3500 cm^{-1} with those of the authentic samples described before.

(d) *Spectroscopy.* The olefin had a band in the infra-red at 1749 cm^{-1}, but no selective absorption in the ultra-violet between 2400 and 3000 Å.

Oxidative degradation of DL-Threo-2H:3H-*hexafluoroadipic acid*

The acid (1·0 g), potassium permanganate (5·0 g), and aqueous potassium hydroxide (30 cc; 1N) were refluxed together for 22 hr. Isolation as usual afforded tetrafluorosuccinic acid (73 per cent), m.p. 112–114° (cited value[8] 115–116°) (Found: equiv., 97. Calc. for $C_4H_2O_4F_4$: equiv., 95), characterised also as the dianilinium salt (50 per cent over-all), m.p. 225–226° (from acetone–chloroform) (Found: C, 51·0; H, 4·3%; equiv., 189).

Characterisation of 4H/5H-*octafluoro*cyclo*hex*-1-*ene*

(a) *Oxidation.* The olefin (2·16 g) was oxidised as usual[11] (at 100°, with no bicarbonate) to give an acidic solid (1·21 g). Distillation of a portion (0·44 g) at 180° (bath temp.)/15 mm onto a cold finger gave the hygroscopic DL-3H:4H-*hexafluoroadipic acid* (0·37 g), m.p. 150–151° (Found: C, 28·2; H, 1·7%; equiv., 126). In a second experiment, the same crude acid (10·5 g) was formed from the olefin (10·4 g).

The acid gave a *dianilinium* salt (56 per cent) (from acetone–chloroform) m.p. 186–187° (Found: C, 49·1; H, 3·9. Calc. for $C_{18}H_{18}O_4N_2F_6$: C, 49·1; H, 4·1%), and a *di-(S-benzylthiuronium)* salt (27 per cent) (from water), m.p. 227–228° (Found: C, 45·4; H, 4·3%).

The crude acid (0·25 g), ethyl alcohol (10 cc), and fluorosulphonic acid (0·5 cc) were refluxed together for 2 hr, the mixture poured into water, and the oily diester extracted with ether. The extracts were separated, dried ($MgSO_4$), filtered, and ammonia passed through for ½ hr. After 15 hr at 10–15°, the ether was distilled off, and the residue recrystallised from water to give the *diamide* (0·08 g), m.p. 206–207° (Found: C, 28·7; H, 2·5. Calc. for $C_6H_6O_2N_2F_6$: C, 28·6; H, 2·4%).

(b) *Addition of chlorine.* 1H:2H-4:5-*Dichlorooctafluoro*cyclo*hexane* (54 per cent), a colourless liquid, b.p. 138–139° (Found: C, 23·3; H, 0·6; F, 50·8. Calc. for $C_6H_2Cl_2F_8$: C, 24·3; H, 0·7; F, 51·2%), was obtained by the usual process.

(c) *Dehydrofluorination.* The olefin (6·0 g), potassium hydroxide (10·0 g) and water (10 cc) were refluxed together for 12 hr. The product was separated, washed, and dried ($MgSO_4$). Analytical gas chromatography showed three components, with retention times corresponding to those of 1H-heptafluoro*cyclo*hexa-1:4-diene, hexafluorobenzene, and the starting material. Separation (4·26 g) by preparative-scale gas chromatography gave the diene (1·66 g), b.p. 67°; hexafluorobenzene (0·54 g), b.p. 80°; and the 4H/5H-ene (1·74 g), b.p. 90°. Over the range 650–3500 cm^{-1} these compounds had infra-red spectra identical with those of authentic specimens.

(d) *Spectroscopy.* There was an infra-red band at 1750 cm^{-1}, but no selective absorption in the ultra-violet.

Oxidative degradation of DL-3H:4H-*hexafluoroadipic acid*

The acid (1·19 g) potassium permanganate (5 g) and aqueous potassium hydroxide (30 cc; 1N) were refluxed together for 19 hr to give an acidic solid (0·95 g). A portion (0·69 g) was distilled at 155° (bath temp.)/15 mm onto a cold finger to give difluoromalonic acid (0·61 g) m.p. 115–116° (cited[8] value 117–118°) (Found: equiv., 71·6. Calc. for $C_3H_2O_4F_2$: equiv., 70·0). The crude acid (0·27 g) gave dianilinium difluoromalonate (0·41 g), m.p. 164–165° (Found: C, 55·2; H, 4·9%; equiv., 164).

Optical resolution of DL-3H:4H-*hexafluoroadipic acid*

A solution of the racemic acid (5·0 g) in ethyl alcohol (100 cc) was added to a solution of L-brucine (15·5 g) in ethyl alcohol (200 cc), and the mixture was boiled, filtered, and set aside. Since a syrup was deposited, the alcohol was evaporated at 15 mm pressure, and the solid residue remaining was dissolved in hot water (100 cc). After 3 days at 10–15° the precipitate (5·61 g) was filtered off from the mother liquor (A) and recrystallised twice from water (25–35 cc) (optical rotation then constant) to give the less soluble diastereoisomeric *di-brucine* salt (3·87 g), m.p. 250° (decomp.) (the specimen softened and water was lost at ca. 185°), $[\alpha]_D^{20} - 12{\cdot}6°$ (*c*, 2·05 in ethanol) (Found: C, 56·8; H, 5·8. Calc. for $C_{52}H_{56}O_{12}N_4F_6$, $3H_2O$: C, 56·9; H, 5·7%).

Concentration of the original mother liquor (A) gave more solid which was filtered off from the new mother liquor (B) and recrystallised five times to give a further crop (1·51 g) of the same diastereoisomer, $[\alpha]_D^{20} - 12{\cdot}5°$ (*c*, 2·08 in ethanol).

A solution of this salt (5·03 g) in warm water (50 cc) was treated with aqueous sodium hydroxide (0·025 N) until just alkaline, and the precipitated brucine (recovery 95 per cent) filtered off. The filtrate was acidified (H_2SO_4) and extracted continuously with ether, the extract dried ($MgSO_4$) and evaporated, to give an acidic solid (1·08 g). Distillation of a portion (0·94 g) at 220–230° (bath temp.)/15 mm onto a cold finger gave the *laevo*-acid (0·66 g) which had $[\alpha]_D^{24} - 17{\cdot}5°$ (*c*, 4·0 in water). The *laevo*-acid (0·20 g) was characterised as the *di-(S-benzylthiuronium)* salt (0·19 g) (from water), m.p. 227–228°, $[\alpha]_D^{24} - 10{\cdot}9°$ (*c*, 1·28 in methanol) (Found: C, 45·1; H, 4·1%).

The mother liquor (B) was concentrated further, and the second diastereoisomeric brucine salt was purified to constant rotation by a systematic fractional crystallisation in which the crops of solid obtained were recrystallised from a mother liquor from which a salt of higher negative rotation had been gained. The more soluble diastereoisomeric *di-brucine* salt (3·15 g) had m.p. 250° (decomp.); (with softening at ca. 195°) $[\alpha]_D^{21} - 1{\cdot}94°$ (*c*, 2·05 in ethanol) (Found: C, 57·1; H, 5·7%).

Treatment of this salt (2·81 g) as before gave a crude acid (0·75 g), part (0·60 g) of which was distilled to afford the *dextro*-acid (0·43 g), $[\alpha]_D^{22} + 16{\cdot}6°$ (*c*, 1·93 in water). The *di-(S-benzylthiuronium)* salt had m.p. 227–228° (from water), $[\alpha]_D^{24} + 9{\cdot}0°$ (*c*, 1·33 in methanol) (Found: C, 45·1; H, 4·1%).

Dehydrofluorination of 1H/2H:4H-*nonafluoro*cyclo*hexane*

The trihydro-compound (45·0 g, b.p. 101°), potassium hydroxide (75 g) and water (75 cc) were refluxed together for 6 hr. The product (31·5 g) showed 6 peaks in analytical gas chromatography with retention times the same as those of the products (i)–(vi) obtained by dehydrofluorination of the stereoisomeric nonafluoro*cyclo*hexane (b.p. 92°). Preparative-scale gas chromatographic separation of the mixture (8·94 g) afforded the following fractions (after distillation from the traps *in vacuo*): (i) (0·67 g), b.p. 66·5–67·0°; (ii) (2·03 g), b.p. 71·5–72·5°; (iii) (0·69 g), b.p. 76°; (iv) (0·81 g), b.p. 80°; (v) (0·35 g), b.p. 85°; and (vi) (3·90 g), b.p. 89–90°. Each of these fractions (i)–(vi) had an infra-red spectrum (over the range 650–3500 cm^{-1}) identical with that of the fraction of similar number isolated from the dehydrofluorination of the nonafluoro*cyclo*hexane, b.p. 92°.

Comparative dehydrofluorinations of the two nonafluorides

A sample (ca. 1 g) of each of the 1H:2H:4H-nonafluoro*cyclo*hexanes (b.p. 92° and 101°) together with 2N-aqueous potassium hydroxide (ca. 10 cc) was shaken in a sealed tube at 45° for ½ hr. The products were analysed by gas chromatography (dinonyl phthalate/kieselguhr 1 : 2, temp. 77°, N_2 flow-rate 1·0 l/hr and tricresyl-phosphate/kieselguhr 1 : 3, temp. 85°, N_2 flow rate 0·9 l./hr; the first packing does not completely separate the 1H:4H/2H-isomer (b.p. 92°) from the 3H/4H-olefin, the second packing does not completely separate the 1H:4H/2H-isomer and the 4H/5H-olefin, but with a run on each packing a complete analysis may be obtained). The 1H:4H/2H-isomer (b.p. 92°) gave very little of the mono-enes and only traces of the dienes, most of the compound being unattacked. Well over half of the 1H/2H:4H-isomer (b.p. 101°) was decomposed. Considerable quantities of the mono-enes were formed, but only small amounts of the dienes.

Reaction of 4H/5H-*octafluoro*cyclo*hex*-1-*ene with lithium aluminium hydride*

The olefin (5·02 g) in diethyl ether (25 cc) was added dropwise during 10 min to a stirred suspension of lithium aluminium hydride (0·88 g) in ether (25 cc) at 0°. After 10 min further, water (25 cc) was added cautiously, followed by sulphuric acid (25 cc, 50 per cent by vol.). The ether layer was separated, dried ($MgSO_4$), and the bulk of the ether distilled off through a 1 ft distillation column packed with gauze spirals. The residue, b.p. $>34°$, in analytical gas chromatography showed 3 peaks (besides that due to ether). These had retention times of 31, 57, and 62 min (6 ft column, dinonyl phthalate/kieselguhr 1 : 2, temp. 99°, N_2 flow-rate 1·0 l./hr). By means of the preparative-scale gas chromatography column (temp. 103°, N_2 flow-rate 9·2 l./hr) three fractions were obtained: (i) ether; (ii) 1H, 4H/5H-*heptafluoro*cyclo*hex*-1-*ene* (1·63 g), a colourless liquid, b.p. 103–104°, n_D^{18} 1·3503 (Found: C, 34·8; H, 1·5. Calc. for $C_6H_3F_7$: C, 34·6: H, 1·45%); (iii) a mixture of two hexafluoro*cyclo*hexenes (1·64 g), b.p. 117–119° (Found: C, 38·0; H, 2·2. Calc. for $C_6H_4F_6$: C, 37·9; H, 2·1%). This was not completely separated under these conditions, and further separation was not attempted.

The heptafluoro-olefin had a C=C band in the infra-red at 1710 cm^{-1}; over the range 650–3500 cm^{-1} the spectrum was identical with that of a heptafluoro*cyclo*hexene obtained from the dehydrofluorination of a 1H:2H:4H:5H-octafluoro*cyclo*hexane,[4] b.p. 119°.

Oxidation of 1H, 4H/5H-*heptafluoro*cyclo*hex*-1-*ene*

Treatment with aqueous permanganate at 85° for 17 hr, followed by working-up as usual, afforded dianilinium DL-3H:4H-hexafluoroadipate (23 per cent), m.p. 189–190° (Found: C, 48·8: H, 4·1%; equiv., 222) and the di-(*S*-benzylthiuronium) salt, m.p. 226–227° (Found: C, 44·9; H, 4·2%).

Dehydrofluorination of 1H, 4H/5H-*heptafluoro*cyclo*hex*-1-*ene*

The olefin (2·92 g) was refluxed for 2½ hr with potassium hydroxide (4·5 g) in water (4·5 cc). The organic layer was separated, washed with water, and dried ($MgSO_4$). Analytical gas chromatography showed 4 peaks, and preparative-scale chromatography afforded 4 fractions; (i) (0·16 g), and (ii) (0·05 g) were hexafluoro*cyclo*hexa-1:4-dienes; (iii) was pentafluorobenzene (0·48 g), b.p. 89°; and (iv) was starting material (1·15 g), b.p. 103–104°. These compounds had infra-red spectra respectively identical with those of the four analogous products[4] from the dehydrofluorination of 1H:2H:4H:5H-octafluoro*cyclo*hexane, b.p. 119°.

Infra-red Spectra

These have been measured[6,7] for all the new compounds described, and the spectra deposited in the Documentation of Molecular Spectra issued by Butterworths. Measurements were made in the vapour state in a 10·1 cm cell over the range 650–3000 cm^{-1}.

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