

922. *Fluorocyclohexanes. Part VIII.*¹ *Lithium Aluminium Hydride Reduction of Decafluorocyclohexene.*

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Decafluorocyclohexene, with lithium aluminium hydride in ether, gave 1*H*- and 3*H*-nonafluorocyclohexene, 1*H*,2*H*- and 1*H*,6*H*-octafluorocyclohexene, and 1*H*,6*H*,6*H*- and 1*H*,2*H*,3*H*-heptafluorocyclohexene by what appears to be an addition-elimination process. These cycloalkenes have been characterised and several new polyfluorocyclohexanes and related compounds have been made from them. Elimination is the most important reaction of such systems, and a possible pathway for a *cis-E2*-process is suggested.

It has been reported² that lithium aluminium hydride reacts with certain fluorinated cyclohexenes, the overall effect being replacement of vinylic fluorine atom by hydrogen. It was then suggested that the hydride behaved as a nucleophilic reagent and that the addition of a negative ion such as $[\text{AlH}_4]^-$ or H^- to the electron-deficient double bond was followed by elimination of $[\text{AlH}_3\text{F}]^-$ or F^- . This behaviour was found first with decafluorocyclohexene which gave a mixture of six compounds. The investigation was referred to previously,² but it has only recently been completed and is now reported fully.

Decafluorocyclohexene (I) with lithium aluminium hydride in ether gave six products (II, III, V, VII, XII, XIII) which were separated by preparative-scale gas chromatography and characterised by oxidation, dehydrofluorination, fluorination, and spectroscopy. The first two compounds to emerge from the chromatography tube were the known 1*H*-³ (II) and 3*H*-nonafluorocyclohexene⁴ (III), the latter only in traces. The third component (V), $\text{C}_6\text{H}_2\text{F}_8$, was converted by potassium permanganate into octafluoro-adipic acid, showing it to be 1*H*,2*H*-octafluorocyclohexene. Support for this structure was provided by infrared and nuclear magnetic resonance (n.m.r.) spectroscopy,⁵ by mass spectrometry,⁶ and by the resistance of the compound to aqueous alkali. Further, saturation of the double bond, by fluorination with cobaltic fluoride, gave 1*H*/2*H*- and 1*H*,2*H*-decafluorocyclohexane. The double bond was also readily saturated by catalytic hydrogenation at atmospheric pressure to give 1*H*,1*H*,2*H*,2*H*-octafluorocyclohexane (IX). This new octafluorocyclohexane was resistant to aqueous alkali under extreme conditions, which underlines the importance of acidity of the hydrogen in dehydrofluorinations of polyfluorocyclohexanes (cf. the 1*H*,2*H*,4*H*,5*H*-octafluorocyclohexanes,⁷ all of which react). With chlorine, compound (V) undergoes both addition and substitution, giving DL-1*H*/2*H*-1,2-dichloro-octafluorocyclohexane (IV) and 2*H*-1,1,2-trichloro-octafluorocyclohexane. The former gave the expected 1*H*,1*H*,2*H*,2*H*-octafluorocyclohexane (IX) with lithium aluminium hydride. The stereochemistry of compound (IV) was established from its n.m.r. spectrum, by means of information obtained from a similar spectrum of 1*H*/2*H*-decafluorocyclohexane. Dehydrohalogenation occurred with aqueous alkali and gave very largely 1*H*-2-chloro-octafluorocyclohexene (VIII) by "inwards" *cis*-elimination of hydrogen chloride with some 2,3-dichlorohexafluorocyclohexa-1,3-diene (X) by "outwards" elimination of hydrogen fluoride. The former was characterised by oxidation to octafluoro-adipic acid and by infrared spectroscopy and mass spectrometry,⁶ the latter by ultraviolet (u.v.) and n.m.r. spectroscopy⁵ and mass spectrometry.⁶

¹ Part VII, Stephens and Wiseman, *J.*, 1963, 2083.

² Nield, Stephens, and Tatlow, *J.*, 1960, 3800.

³ Roylance, Tatlow, and Worthington, *J.*, 1954, 4426.

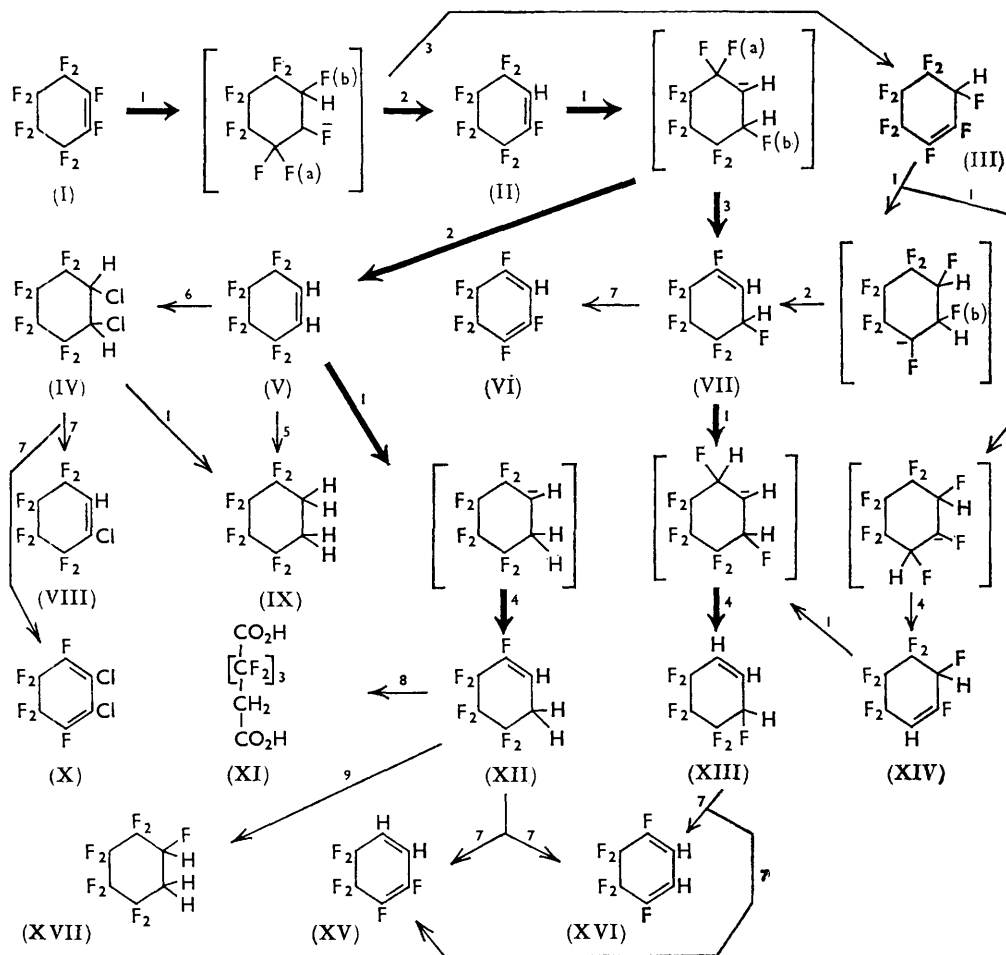
⁴ Evans and Tatlow, *J.*, 1955, 1184; Evans, Godsell, Stephens, Tatlow, and Wiseman, *Tetrahedron*, 1958, 2, 183.

⁵ Thomas, personal communication.

⁶ Majer, personal communication.

⁷ Nield, Stephens, and Tatlow, *J.*, 1959, 159; Smith and Tatlow, *J.*, 1957, 2505; Stephens, Tatlow, and Wiseman, *J.*, 1959, 148

With compound (IV), as in earlier work,^{2,7} the sterically unfavourable "inwards" *cis*-elimination predominates. Presumably it is favoured by the lower stability of the monohalogenomethylene group (in this case $>CHCl$) than of the difluoromethylene group, and with compound (IV) especially so since chlorine is a better "leaving group" than fluorine. This *cis*-elimination is analogous to that occurring in the dehydrochlorination



Reagents: 1, $LiAlH_4$; 2, loss of F(b) as F^- ; 3, loss of F(a) as F^- ; 4, loss of F^- ; 5, H_2 -Pd; 6, Cl_2 ; 7, KOH; 8 $KMnO_4$; 9, CoF_3 .

(Pathway of C_6F_{10} - $LiAlH_4$ reaction traced by thick arrows.)

of the all *trans*-1Cl,3Cl,5Cl/2Cl,4Cl,6Cl-cyclohexane⁸ (β -isomer) for which $E1cB$ ⁹ and $E2$ ¹⁰ mechanisms have been proposed. Recent studies,¹¹ however, show that *cis*-coplanar $E2$ eliminations occur readily in cyclopentane systems and it is possible that the very

⁸ Cristol, *J. Amer. Chem. Soc.*, 1947, **69**, 338.

⁹ Cristol, Hause, and Meek, *J. Amer. Chem. Soc.*, 1951, **73**, 674; Cristol and Fix, *ibid.*, 1953, **75**, 2647.

¹⁰ Hughes, Ingold, and Pasternak, *J.*, 1953, 3832.

¹¹ DePuy, Thurn, and Morris, *J. Amer. Chem. Soc.*, 1962, **84**, 1314; Heitzman, Patrick, Stephens, and Tatlow, *J.*, 1963, 281; Le Bel, Karger, Powers, and Subramanian, Abs. 142nd Meeting Amer. Chem. Soc., 1962, p. 101Q; Stephens and Wiseman, *J.*, 1963, 2083.

difficult *cis*-eliminations in cyclohexanes occur by a concerted process involving a *cis*-coplanar system in a boat conformation. Only in the case of the hexachlorocyclohexanes are kinetic measurements available,^{9,10} and these indicate an extra 12 kcal./mole in activation energy for the *cis*-elimination. Although no values are available for the energy barrier between the chair and the boat forms in substituted cyclohexanes of the type considered, 12 kcal./mole is not an unreasonably small value (the energy difference between the chair and the boat form of cyclohexane is 5.5 kcal./mole¹² and the energy barrier to rotation in perfluorocyclohexane is given as 9.9 kcal./mole¹³).

The fourth component (VII) of the original reaction mixture was an octafluorocyclohexene, and oxidation with potassium permanganate in water containing sodium hydrogen carbonate gave 2*H*-heptafluoroadipic acid,⁴ which was characterised as its bis-*S*-benzylthiuronium salt; as in earlier work,⁴ the dianilinium salt was not very stable. Various other oxidation conditions gave a mixture of hexafluoroglutaric and tetrafluorosuccinic acid. The presence of $-\text{CH}=\text{>CH}$, and $-\text{CH}=\text{CF}-$ groups was indicated by i.r. absorption peaks at 3070, 2950, and 1710 cm^{-1} , respectively. Dehydrofluorination of this component (VII) gave only the known⁷ 2*H*-heptafluorocyclohexa-1,3-diene (VI). This, of course, would result from 1,2- and 1,4-elimination. Fluorination of component (VII) with cobaltic fluoride gave perfluorocyclohexane, 1*H*-nonafluorocyclohexene, and 1*H*/2*H*- and 1*H*,2*H*/-decafluorocyclohexane. All this evidence shows that component (VII) is 1*H*,6*H*-octafluorocyclohexene; this structure is consistent with its n.m.r. spectrum⁵ and its mass-spectral fragmentation pattern.⁶

The longest-retained component of the original reaction mixture was found by mass spectrometry⁶ to be a 5 : 1 mixture of two heptafluorocyclohexenes that could not be separated. However, 1*H*,2*H*- (V) and 1*H*,6*H*-octafluorocyclohexene (VII) with lithium aluminium hydride in ether gave pure specimens of two olefins (XII and XIII, respectively), and i.r. spectroscopy showed that both were present in the mixture. This method of preparation also provides evidence for their structures and mode of formation.

The heptafluorocyclohexene (XII) made from 1*H*,2*H*-octafluorocyclohexene (V) was oxidised by acid permanganate at room temperature to crystalline 2*H*,2*H*-hexafluoroadipic acid (XI). However, in the absence of acid or with permanganate in acetone the latter acid was obtained in only small yield, together with tetrafluorosuccinic and hexafluoroglutaric acid which were separated by fractional crystallisation of the anilinium salts. It was of interest to find that the hexafluoroadipic acid (XI) gave a monoanilinium salt, which presumably reflects the lower acidity of the carboxyl group attached to the methylene group.

In the i.r. spectrum of compound (XII) absorption peaks at 3050, 2950, and 1710 cm^{-1} are ascribed to $-\text{CH}=\text{>CH}$, and $-\text{CH}=\text{CF}-$ groups, respectively. Dehydrofluorination gave 1*H*,2*H*- (XV)⁷ and the new 2*H*,3*H*-hexafluorocyclohexa-1,3-diene (XVI). The latter displayed strong selective absorption in the u.v. region, oxidation gave tetrafluorosuccinic acid, pyrolytic defluorination¹⁴ gave penta- and 1,2,3,4-tetra-fluorobenzene, and the ¹⁹F and ¹H n.m.r. spectra⁵ were consistent with the structure so indicated. Reaction with cobaltic fluoride gave the known 1*H*/2*H*- and 1*H*,2*H*/-decafluorocyclohexane and the new 1*H*,1*H*,2*H*-nonafluorocyclohexane (XVII) which was identified by an unambiguous alternative synthesis from 1*H*-nonafluorocyclohexene. The latter olefin was converted into a mixture of the known¹⁵ *cis*- and *trans*-1*H*-1,2-dichlorononafluorocyclohexane by addition of chlorine, and this mixture was reduced with lithium aluminium hydride to the desired nonafluorocyclohexane.

Compound (XII) must obviously be 1*H*,6*H*,6*H*-heptafluorocyclohexene and this assignment was confirmed by the ¹⁹F n.m.r. spectrum⁵ and the fragmentation pattern

¹² Johnson, Bauer, Margrave, Frisch, Dreger, and Hubbard, *J. Amer. Chem. Soc.*, 1961, **83**, 606.

¹³ Tiers, *Proc. Chem. Soc.*, 1960, 389.

¹⁴ Coe, Patrick, and Tatlow, *Tetrahedron*, 1960, **9**, 240.

¹⁵ Lancashire, Stephens, and Tatlow, unpublished work.

obtained on mass-spectral analysis.⁶ Mass spectrometry also showed that this olefin constituted 83% of the mixed component obtained on reduction of decafluorocyclohexene by lithium aluminium hydride.

The dehydrofluorination of 1*H*,1*H*,2*H*-nonafluorocyclohexane (XVII) is of interest when considered in conjunction with the aforementioned alkali-resistant 1*H*,1*H*,2*H*,2*H*-octafluorocyclohexane (IX) in that it is an example of the interplay of C-F bond strength and hydrogen "acidity" in such eliminations. Thus, the predominant product from (XVII), 1*H*,2*H*-octafluorocyclohexene (V), arises by loss of fluorine from the >CHF group which involves attack by base on the presumably less acidic hydrogen of the >CH₂ group. The trace of 1*H*-nonafluorocyclohexene also found almost certainly arises from a small amount of chlorononafluorocyclohexane, the intermediate reduction product.

1*H*,6*H*-Octafluorocyclohexene (VII) and lithium aluminium hydride gave predominantly a heptafluorocyclohexene (XIII), together with two other components which were not obtained pure and presumably arose from further attack of the reducing agent on the olefin (XIII).

The heptafluorocyclohexene (XIII) displayed a very weak i.r. absorption band at 1690 cm.⁻¹ associated with the -CH=CH- group in this type of molecule. Dehydrofluorination with aqueous alkali gave 1*H*,2*H*- (XV) and 2*H*,3*H*-hexafluorocyclohexa-1,3-diene (XVI). Thus compound (XIII) must be 1*H*,2*H*,3*H*-heptafluorocyclohexene and this was confirmed by the ¹⁹F n.m.r. spectrum⁵ and the fragmentation pattern on mass-spectral analysis.⁶

Thus, the depicted pathway for the reaction of decafluorocyclohexene with lithium aluminium hydride is clearly demonstrated. Further reduction would be expected and almost certainly occurs, until the double bond is completely deactivated to nucleophilic attack; *e.g.*, it is known² that the related 1,4,4,5,5,6- and 1,4,4,5,6,6-hexafluorocyclohexenes do not react with an excess of lithium aluminium hydride even on prolonged heating. It was of interest that elimination of fluorine from the >CHF group occurred more readily than from >CF₂ in each of the postulated intermediate products; this effect was noted in earlier work² when 4*H*/5*H*-1,3,3,4,5,6,6-heptafluorocyclohexene and lithium aluminium hydride produced about twice as much 4*H*/5*H*-3,3,4,5,6,6-hexafluorocyclohexene (loss of F from >CHF) as the 5*H*,6*H*-1,3,4,4,5,6-hexafluorocyclohexenes (loss of F from >CF₂). With decafluorocyclohexene (I), 1*H*-nonafluorocyclohexene (II) (loss of F from >CHF) was apparently formed in about fifty times the amount of its 3*H*-isomer (III) (loss of F from >CF₂). However, from the subsequent reaction of 1*H*-nonafluorocyclohexene itself with ethereal lithium aluminium hydride, 1*H*,2*H*-octafluorocyclohexene (V) (loss of F from >CHF) and its 1*H*,6*H*-isomer (VII) (loss of F from >CF₂) were formed in the approximate ratio of 3 : 1. Part of the apparent difference in relative ease of elimination from C₆F₁₀ almost certainly lies in the fact that 3*H*-nonafluorocyclohexene (III) reacts with lithium aluminium hydride more rapidly than does 1*H*-nonafluorocyclohexene (II). When 3*H*-nonafluorocyclohexene (III) was treated with lithium aluminium hydride in ether in the usual way, the products separated by gas chromatography were 1*H*,3*H*-octafluorocyclohexene (XIV), 1*H*,6*H*-octafluorocyclohexene (VII), and 1*H*,2*H*,3*H*-heptafluorocyclohexene (XIII), all displaying correct i.r. spectra. Thus, the pattern of behaviour is of the type already considered. The initial attack of the reagent is predominantly at C-2 of the olefin, as would be expected since a >CF₂ group should have a more powerful inductive attraction than >CHF on the double-bond electrons.

The olefin (XIV) was not detected in the product from lithium aluminium hydride and decafluorocyclohexene, presumably owing to the small quantity present and chromatographic overlap.

EXPERIMENTAL

Techniques.—Oxidations, gas chromatography, and infrared measurements were carried out as before,⁷ unless otherwise stated. Known acids were characterised by two derivatives which had correct elemental analyses in each case reported.

Reaction of Decafluorocyclohexene with Lithium Aluminium Hydride.—Decafluorocyclohexene ³ (I) (224.5 g.) was added dropwise during 1½ hr. to a stirred suspension of lithium aluminium hydride (21.0 g.) in diethyl ether (300 c.c.) at -20°. When the initial reaction had subsided, the solution was refluxed for 1 hr., then cooled to -20°, and 50% v/v sulphuric acid (200 c.c.) was added dropwise, followed by water (200 c.c.) until no precipitate remained. The dried (MgSO₄) ethereal solution was evaporated through a vacuum-jacketed column (1' × ½") packed with glass helices to leave a mixture of fluorocyclohexenes (180 g.) which was separated by preparative gas chromatography (column B, 100°, N₂ flow-rate 60 l./hr.), to give the following (in order of emergence from column): (i) 1*H*-nonafluorocyclohexene (II) (41.4 g.), b. p. 64°, with a correct infrared spectrum; ³ (ii) 3*H*-nonafluorocyclohexene (III) (0.7 g.), b. p. 70°, with a correct infrared spectrum; ⁴ (iii) 1*H*,2*H*-octafluorocyclohexene (V) (46.2 g.), b. p. 86° (Found: C, 31.6; H, 0.7. C₆H₂F₈ requires C, 31.9; H, 0.9%); (iv) 1*H*,6*H*-octafluorocyclohexene (VII) (19.4 g.), b. p. 88° (Found: C, 31.9; H, 1.0%); (v) a mixture of 1*H*,6*H*,6*H*- (XII) and 1*H*,2*H*,3*H*-heptafluorocyclohexene (XIII) (32.2 g.), b. p. 114°, mass spectroscopy indicating the presence of 83% of the former.⁶ 1*H*-Nonafluorocyclohexene prepared in this way contained a trace of ether which was removed by a second gas-chromatographic separation in a column of type A packed with tritoyl phosphate-kieselguhr (1 : 3).

Characterisation of 1H,2H-Octafluorocyclohexene (V).—(a) *Oxidation.* The olefin (1.5 g.), potassium permanganate (15.0 g.), and water (60 c.c.) in a rocking autoclave at 85° for 18 hr. gave octafluoroadipic acid (35%).

(b) *Spectroscopy.* The olefin showed characteristically weak absorptions at 1695 and 1725 cm.⁻¹ ascribable to a -CH=CH- group. The ¹⁹F n.m.r. spectrum was consistent with the assigned structure.⁵ Mass spectrometry ⁶ revealed a total mass peak of 226 (*M*, 226) and the expected fragmentation pattern.

(c) *Resistance to alkali.* The olefin was unaffected by prolonged refluxing with concentrated potassium hydroxide solution.

(d) *Fluorination.* The olefin (3.0 g.) was fluorinated in a small static cobaltic fluoride reactor ⁷ and gave a solid product (2.1 g.) which was shown by gas chromatography to contain two components with retention times identical with those of 1*H*/2*H*- and 1*H*,2*H*/-decafluorocyclohexanes.

1*H*,1*H*,2*H*,2*H*-Octafluorocyclohexane (IX).—The olefin (V) (5.2 g.) absorbed hydrogen at atmospheric pressure at 15° in the presence of palladium (5%) on asbestos to give, after gas chromatography (column A), 1*H*,1*H*,2*H*,2*H*-octafluorocyclohexane (IX) (2.7 g.), m. p. 54–55°, b. p. 107° (Found: C, 31.6; H, 1.8. C₆H₄F₈ requires C, 31.6; H, 1.8%). Mass spectrometry gave a total mass peak of 228 (*M*, 228); there was an infrared absorption at 2980 cm.⁻¹ (>CH), and the n.m.r. spectrum was consistent with the assigned structure.⁵ The compound was unaffected when refluxed with an equal volume of concentrated potassium hydroxide solution or shaken with this reagent for 10 hr. at 100°.

DL-1*H*/2*H*-1,2-Dichloro-octafluorocyclohexane (IV).—The olefin (V) (45.0 g.) and chlorine (ca. 16 g.) in a sealed Pyrex tube were irradiated with u.v. light for 48 hr. at 15°. After removal of the excess of chlorine the product (52.6 g.) was separated by gas chromatography (column B) to give: (i) starting material (5.7 g.); (ii) DL-1*H*/2*H*-1,2-dichloro-octafluorocyclohexane (IV) (34.4 g.), b. p. 123° [Found: C, 24.5; H, 0.6; Cl, 23.4%; *M* (mass spectrometry), 296.9. C₆H₂Cl₂F₈ requires C, 24.3; H, 0.7; Cl, 23.9%; *M*, 296.9]; the ¹⁹F magnetic resonance spectrum was characteristic of a 1,2-diaxial arrangement as found in 1*H*/2*H*-decafluorocyclohexane; ¹⁶ (iii) 1*H*-1,2,2-trichloro-octafluorocyclohexane (4.2 g.) [Found: C, 22.6; H, 0.3%; *M* (mass spectrometry), 331.4. C₆HCl₃F₈ requires C, 21.7; H, 0.3%; *M*, 331.4].

DL-1*H*/2*H*-1,2-Dichloro-octafluorocyclohexane (IV) (10.5 g.) and lithium aluminium hydride (2.6 g.) in ether (100 c.c.) gave 1*H*,1*H*,2*H*,2*H*-octafluorocyclohexane (IX) (4.6 g.) with a correct infrared spectrum.

DL-1*H*/2*H*-1,2-Dichloro-octafluorocyclohexane (IV) (34.4 g.), potassium hydroxide (25 g.), and water (50 c.c.) were refluxed together for 4 hr. The organic product (27.9 g.) was separated by gas chromatography (column B) into the following components: (i) 1*H*-2-chloro-octafluorocyclohexene (VIII) (21.6 g.) b. p. 95° (Found: C, 27.9; H, 0.3; Cl, 13.6. C₆HClF₈ requires C, 27.7; H, 0.4; Cl, 13.6%); (ii) 2,3-dichlorohexafluorocyclohexa-1,3-diene (X) (1.3 g.); and (iii) a trace of starting material. Mass spectrometry of compound (VIII) showed a total mass of 260.5 (*M*, 260.5) and the expected fragmentation pattern; ⁶ there was an infrared absorption

¹⁶ Homer, Ph.D. Thesis, University of Birmingham; Homer and Thomas, unpublished work.

at 1660 cm^{-1} ($-\text{CH}=\text{CCl}-$), and oxidation gave octafluoroadipic acid. Mass spectrometry of compound (X) gave a total mass peak of 256.9 (M , 256.9) and the expected fragments; ⁶ the ¹⁹F n.m.r. spectrum was consistent with the assigned structure; ⁵ and light absorption in ethanol revealed a peak at 2740 Å (ϵ 1.7×10^3).

Characterisation of 1H,6H-Octafluorocyclohexene (VII).—(a) *Oxidation.* The olefin (0.5 g.), potassium permanganate (0.7 g.), water (30 c.c.), and sodium hydrogen carbonate (1.5 g.) were shaken together at 15° for 48 hr. The usual isolation procedure gave crude 2H-heptafluoroadipic acid (0.5 g.) which formed an unstable anilinium salt (0.5 g.) but this in turn gave bis-*S*-benzylthiuronium 2H-heptafluoroadipate, m. p. 230—232° (lit.,⁴ 232—233°) (Found: C, 43.7; H, 3.8. Calc. for $\text{C}_{22}\text{H}_{23}\text{F}_7\text{O}_4\text{N}_4\text{S}_2$: C, 43.7; H, 3.8%). However, this oxidation was difficult to reproduce and under most reaction conditions tried gave hexafluoroglutaric and tetrafluorosuccinic acid.

(b) *Dehydrofluorination.* The olefin (3.0 g.), potassium hydroxide (2.0 g.), and water (6 c.c.) were shaken together in a sealed Pyrex tube at 100° for 2 hr. Separation of the product (1.4 g.) by gas chromatography (column A) gave starting material (0.9 g.) and 2H-heptafluorocyclohexa-1,3-diene (0.2 g.) with a correct infrared spectrum.

(c) *Fluorination.* The olefin (4.0 g.) was passed over cobaltic fluoride at 50° in a stream of nitrogen (6 l./hr.). The product (2.2 g.) was separated by gas chromatography (column A) into undecafluorocyclohexane, 1H-nonafluorocyclohexene, and 1H/2H-decafluorocyclohexane, all with correct infrared spectra; two minor compounds were identified from their retention times as perfluorocyclohexane and 1H,2H-decafluorocyclohexane.

1H,6H,6H-Heptafluorocyclohexene (XII).—1H,2H-Octafluorocyclohexene (V) (38.2 g.) and lithium aluminium hydride (9.55 g.) in ether were treated in the manner described earlier and gave only 1H,6H,6H-heptafluorocyclohexene (XII) (19.4 g.), b. p. 115° (Found: C, 34.6; H, 1.4. $\text{C}_6\text{H}_3\text{F}_7$ requires C, 34.6; H, 1.4%); it was shown to have the same retention time as the mixed component obtained from decafluorocyclohexene and lithium aluminium hydride, and infrared spectroscopy confirmed its presence in this mixture.

Characterisation of 1H,6H,6H-Heptafluorocyclohexene (XII).—(a) *Oxidation.* (i) The olefin (7.0 g.), potassium permanganate (7.0 g.), water (400 c.c.), and concentrated sulphuric acid (50 c.c.) were intimately mixed by means of a vibrator-type stirrer at 15° for 7 hr. Subsequent treatment was normal and gave a solid acid (8.5 g.) which sublimed at 125—130°/0.05 mm. to give 2H,2H-hexafluoroadipic acid (XI) (4.9 g.), m. p. 115° (Found: C, 28.2; H, 1.8%; Equiv., 127. $\text{C}_6\text{H}_4\text{F}_6\text{O}_4$ requires C, 28.3; H, 1.6%; Equiv., 127) [*bis-S*-benzylthiuronium salt, m. p. 195° (Found: C, 44.6; H, 4.0. $\text{C}_{22}\text{H}_{24}\text{F}_6\text{O}_4\text{N}_4\text{S}_2$ requires C, 45.0; H, 4.1%). (ii) Using permanganate in acetone in the usual way yielded a mixture of tetrafluorosuccinic, hexafluoroglutaric, and 2H,2H-hexafluoroadipic acid which were separated by fractional crystallisation of the anilinium salts. The last-named acid was obtained as the *monoanilinium salt* (4.3%), m. p. 141° (Found: C, 41.3; H, 3.2; Equiv., 172. $\text{C}_{12}\text{H}_{11}\text{F}_6\text{O}_4\text{N}$ requires C, 41.5; H, 3.2%; Equiv., 173.5).

(b) *Fluorination.* The olefin (5.2 g.) was treated with cobaltic fluoride in the previously described manner ⁷ at 70—80° and a N_2 flow-rate of 2 l./hr., to give a solid which was separated by gas chromatography (column A) into the known 1H/2H- (\sim 0.01 g.) and 1H,2H-decafluorocyclohexane (\sim 0.01 g.) with correct infrared spectra, and 1H,1H,2H-nonafluorocyclohexane (XVII) (0.12 g.), m. p. 35—36°, b. p. 91° [Found: C, 23.7; H, 1.1%; M (mass spectrometry), 246. $\text{C}_6\text{H}_3\text{F}_9$ requires C, 29.2; H, 1.2%; M , 246].

1H,1H,2H-Nonafluorocyclohexane (XVII).—1H-Nonafluorocyclohexene (15.0 g.) and chlorine (*ca.* 4.5 g.) were kept together in a sealed tube under u.v. irradiation for 23 hr. to give a mixture (18.5 g.) of *cis*- (1 part) and *trans*-1H-1,2-dichlorononafluorocyclohexane (9 parts) with a correct infrared spectrum.¹⁵ A portion (14.5 g.) and lithium aluminium hydride (1.87 g.) in ether (150 c.c.) in the usual way gave 1H,1H,2H-nonafluorocyclohexane (5.95 g.; purified by gas chromatography), m. p. 35°, b. p. 91°, as the sole product. The infrared spectrum was identical with that of the compound prepared in the above fluorination.

Dehydrofluorination of 1H,1H,2H-Nonafluorocyclohexane (XVII).—The nonafluoride (2.3 g.), potassium hydroxide (10 g.), and water (10 c.c.) were shaken together in a sealed tube at 100° for 5 hr., at the end of which the aqueous phase was pale yellow. The organic layer (1.4 g.) was separated by gas chromatography (column A) to give 1H-nonafluorocyclohexene (trace), 2H-heptafluorocyclohexa-1,3-diene (trace), and 1H,2H-octafluorocyclohexene (0.95 g.); all had correct infrared spectra.

Dehydrofluorination of 1H,6H,6H-Heptafluorocyclohexene (XII).—The olefin (4.0 g.), potassium hydroxide (50.0 g.), and water (22 c.c.) were refluxed together for 6 hr. The product (2.2 g.) was separated by gas chromatography (column A) to give: (i) 1H,2H-hexafluorocyclohexa-1,3-diene (XV) (0.25 g.) with a correct infrared spectrum; (ii) 2H,3H-hexafluorocyclohexa-1,3-diene (XVI) (0.55 g.), b. p. 98° (Found: C, 38.4; H, 1.0. C₆H₂F₆ requires C, 38.3; H, 1.1%), λ_{max} 2660 (ϵ 3.3 \times 10³ in EtOH). The ¹⁹F and ¹H n.m.r. spectra were consistent with the assigned structure.⁵ Oxidation in the usual way gave tetrafluorosuccinic acid and pyrolysis over iron gauze at 490° and a N₂ flow-rate of 2.2 l./hr. gave an ~1 : 4 mixture of pentafluoro- and 1,2,3,4-tetrafluoro-benzene with starting material (0.7 g.).

1H,2H,3H-Heptafluorocyclohexene (XIII).—1H,6H-Octafluorocyclohexene (VII) (23.5 g.) and lithium aluminium hydride (4.21 g.) in ether reacted at -20° and the excess of hydride was then destroyed. The liquid product (26 g.), containing a little ether, was separated into three components (excluding ether) by gas chromatography (column B) but only the shortest-retained one was pure; it was 1H,2H,3H-heptafluorocyclohexene (XIII) (12.4 g.), b. p. 113° (Found: C, 34.4; H, 1.6; F, 64.5. C₆H₃F₇ requires C, 34.6; H, 1.4; F, 64.0%), with a retention time identical with that of the mixed component of the reaction of decafluorocyclohexene and lithium aluminium hydride; infrared spectroscopy confirmed its presence in this mixture.

Characterisation of 1H,2H,3H-Heptafluorocyclohexene (XIII).—(a) *Spectroscopy.* The infrared spectrum displayed a very weak absorption peak at 1690 cm.⁻¹ (-CH=CH-; cf. 1H,2H-octafluorocyclohexene). The ¹⁹F n.m.r. spectrum was consistent with the assigned structure,⁵ as was the mass spectrum⁶ (Total mass 208. *M*, 208]).

(b) *Dehydrofluorination.* The olefin (7.6 g.), potassium hydroxide (9.0 g.), and water (20 c.c.) were refluxed together for 1½ hr. The organic layer (6.15 g.) was washed with water, dried (MgSO₄), and separated by gas chromatography (column A) to give 1H,2H- (XV) (0.75 g.) and 2H,3H-hexafluorocyclohexa-1,3-diene (XVI) (1.45 g.) and starting material (3.32 g.), all with correct infrared spectra.

Reaction of 3H-Nonafluorocyclohexene (III) with Lithium Aluminium Hydride.—A suspension of lithium aluminium hydride (0.2 g.) in ether was added dropwise to a stirred solution of 3H-nonafluorocyclohexene (2.0 g.) in ether, and the mixture was then stirred for 5 min. and treated in the previously described manner, to give: (i) 1H,3H-octafluorocyclohexene (XIV) (0.1 g.); (ii) 1H,6H-octafluorocyclohexene (VII) (0.7 g.); and (iii) 1H,2H,3H-heptafluorocyclohexene (XIII) (0.2 g.); all had correct infrared spectra.

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