754. *Fluorocyclohexanes. Part VI.* Some Hexa- and Pentafluorocyclohexenes and Their Dehydrofluorination.*

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

4H/5H-1,3,3,4,5,6,6-Heptafluorocyclohexene gave, with lithium aluminium hydride in ether, *4H/5H*-3,3,4,5,6,6-hexafluorocyclohexene, *5H/6H*-1,4,4,5,6-pentafluorocyclohexene and *5H/6H*-1,3,4,4,5,6-hexafluorocyclohexene. The first product afforded 1,2,3,4-tetrafluorobenzene on dehydrofluorination, the second gave 1,2,4-trifluorobenzene, and the third all three tetrafluorobenzenes. 3,3,4,4,5,6,6-Heptafluorocyclohexene reacted with lithium aluminium hydride in ether to give 1,4,4,5,5,6- and 1,4,4,5,6,6-hexafluorocyclohexene, which on dehydrofluorination gave 1,2,3,4-tetrafluorobenzene.

When this work was started, ten of the twelve possible fluorobenzenes had been made, mono-,[1] *o*-, *m*-, and *p*-di-,[2] 1,2,4-[3] and 1,3,5-tri-,[4] and 1,2,4,5-[5] and 1,2,3,5-tetra-fluorobenzene[6] by the Balz–Schiemann route, pentafluorobenzene[7] by dehydrofluorination, and hexafluorobenzene by three methods.[8,9,10]. We planned syntheses of the two missing members by addition–elimination reactions[11] of lithium aluminium hydride with fluorocyclohexenes, a process already developed in this Department for one preparation of pentafluorobenzene.[12] This paper describes syntheses of 1,2,3,4-tetrafluorobenzene based on this reaction. However, in the meantime, other routes to this compound have been found, one by Finger's group,[13] one by Wall's,[14] and one in this Department[15] by application, to cyclohexenes or cyclohexadienes with *1H,2H*-atoms, of the new defluorination technique[16] for the synthesis of fluoro-aromatic compounds.

In the reaction of fluorinated olefins with lithium aluminium hydride in diethyl ether the overall effect[11] is the replacement of vinylic fluorine by hydrogen. Lithium aluminium hydride is presumably behaving as a nucleophilic reagent, the double bond

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* Part V, *J.*, 1959, 159.

[1] Balz and Schiemann, *Ber.*, 1927, **60**, 1186; Booth and Martin, "Boron Trifluoride and its Derivatives," John Wiley & Sons, London, 1949; Roe, "Organic Reactions," 1949, Vol. V, 193.

[2] Schiemann and Pillarsky, *Ber.*, 1929, **62**, 3035.

[3] Schiemann, *J. prakt. Chem.*, 1934, **140**, 97.

[4] Finger, Reed, and Finerty, *J. Amer. Chem. Soc.*, 1951, **73**, 153.

[5] Finger, Reed, Burness, Fort, and Blough, *J. Amer. Chem. Soc.*, 1951, **73**, 145.

[6] Finger, Reed, and Oesterling, *J. Amer. Chem. Soc.*, 1951, **73**, 152.

[7] Stephens and Tatlow, *Chem. and Ind.*, 1957, 821; Nield, Stephens, and Tatlow, *J.*, 1959, 166.

[8] McBee, Lindgren, and Ligett, *Ind. Eng. Chem.*, 1947, **39**, 378.

[9] Désirant, *Bull. Classe Sci., Acad. roy. Belg.*, 1955, **41**, 759.

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

[11] Evans and Tatlow, unpublished work.

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

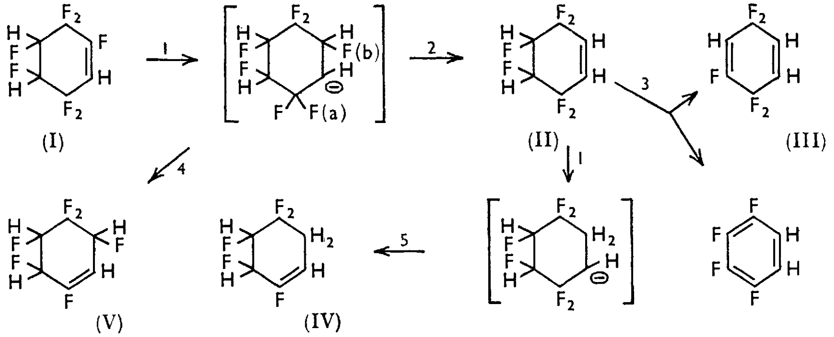
[13] Finger and his co-workers, personal communication.

[14] Pummer, Florin, and Wall, *J. Res. Nat. Bur. Stand.*, 1959, **62**, 113.

[15] Coe, Patrick, and Tatlow, *Tetrahedron*, 1960, **9**, 240.

[16] Gething, Patrick, Tatlow, Banks, Barbour, and Tipping, *Nature*, 1959, **183**, 586.

being attacked by a negative ion, which could be the $[AlH_4]^-$ ion, or the hydride ion H^-. The formation of a new double bond then occurs by elimination of fluorine either as a complex ion such as $[AlH_3F]^-$ or as fluoride ion. The fluorine appears to be lost preferentially from the carbon to which the hydrogen has become attached, but can also come from a $>CF_2$ group.



Reagents: 1, AlH_4^-; 2, loss of F(b) as F^-; 3, KOH; 4, loss of F(a) as F^-; 5, loss of F^-.

An obvious route to precursors of 1,2,3,4-tetrafluorobenzene was the further reaction of 4*H*/5*H*-1,3,3,4,5,6,6-heptafluorocyclohexene (I), which was available from the sequence mentioned above [12] or, more readily, by dehydrofluorination of the 1,1,2,3,4,4,5,6-octafluorocyclohexanes formed in the partial fluorination of benzene.[17] The reaction of the heptafluorocyclohexene (I) with lithium aluminium hydride in diethyl ether gave a mixture of three compounds which were separated by gas chromatography and characterised by oxidation, dehydrofluorination, and spectroscopy. The first compound, a hexafluorocyclohexene (II), gave with potassium permanganate in acetone the known [12] (±)-3*H*,4*H*-hexafluoroadipic acid. The olefin (II) was transparent in the ultraviolet region but displayed a characteristically very weak infrared absorption at 1700 $cm.^{-1}$ attributable to a –CH=CH– group.[18] The structure (II) is thus proved. The compound is identical with material obtained [17] in very small yield from the complex mixture formed by reaction of benzene with cobaltic fluoride. In agreement with this structure it gave with aqueous potassium hydroxide the pentafluoro-diene (III) and 1,2,3,4-tetrafluorobenzene. The product (III) was identified by oxidation to difluoromalonic acid, the absence of selective ultraviolet absorption, and the presence of infrared bands at 1676 and 1729 $cm.^{-1}$ characteristic, respectively, of –CH=CH– and –CH=CF– groups.[18] 1,2,3,4-Tetrafluorobenzene was identified by analysis and by its infrared and ultraviolet absorption. The infrared absorption differed from those of 1,2,3,5- and 1,2,4,5-tetrafluorobenzene, and was later shown to be identical with that of a specimen prepared by Wall's group.[14] 2,3,4,5-Tetrafluorobenzenesulphonic acid was prepared as white very hygroscopic crystals by reaction with stabilised sulphur trioxide at room temperature. 1,2-Dibromotetrafluorobenzene was made with bromine in sulphuric acid [19] and characterised by spectroscopy.

The second component (IV) formed by reaction of lithium aluminium hydride with compound (I) was a pentafluorocyclohexene, and with potassium permanganate gave a crystalline tetrafluoroadipic acid. The presence of a –CH=CF– and a $>CH_2$ group in the cyclohexene (IV) was indicated by infrared peaks at 1710 [18] and 2859 $cm.^{-1}$, respectively. Dehydrofluorination afforded only 1,2,4-trifluorobenzene.[3] Further, this cyclohexene was the sole product of reaction of the hexafluorocyclohexene (II) with ethereal lithium aluminium hydride, demonstrating that it had a 1*H*,2*H*,4*H*,5*H*-unit. All this evidence

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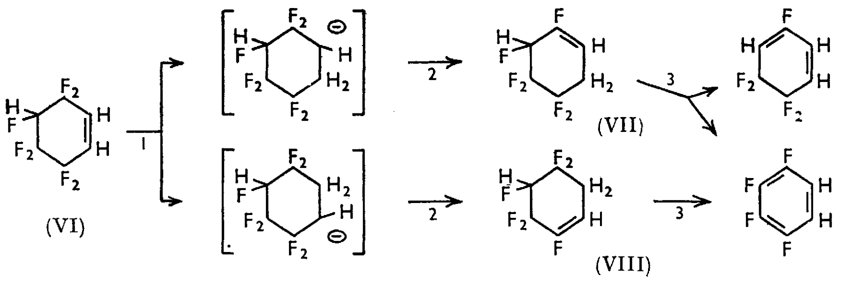
[17] Nield, Stephens, and Tatlow, *J.*, 1959, 159.
[18] Burdon and Whiffen, *Spectrochim. Acta*, 1958, **12**, 139.
[19] Hellmann and Bilbo, *J. Amer. Chem. Soc.*, 1953, **75**, 4590.

shows that compound (IV) was *5H*,*6H*-1,4,4,5,6-pentafluorocyclohexene and that therefore the adipic acid derived from it was the αββ′β′-tetrafluoro-acid.

The third component (V) of the original reaction mixture was a hexafluorocyclohexene and was oxidised by potassium permanganate to a pentafluoroadipic acid. It also displayed an infrared absorption band associated with a $-CH=CF-$ double bond.[18] Dehydrofluorination gave all three tetrafluorobenzenes, which were separated by gas chromatography and identified by infrared spectroscopy. Reaction with cobaltic fluoride under mild conditions [20] was used to saturate the double bond. Three octafluorocyclohexanes [17] were obtained, the *1H*,*2H*,*4H*/*5H*-, *1H*,*5H*/*2H*,*4H*- and *1H*,*4H*/*2H*,*5H*-stereoisomers. The compound (V) must therefore have been 1,3,4,4,5,6-hexafluorocyclohexene. The isolation of the three octafluorocyclohexanes means, however, that two stereoisomers, *3H*,*6H*/*5H*- and *3H*,*5H*/*6H*-, were present. No indication of the presence of two compounds in the material was given by analytical gas chromatography, though two would be expected from the method of synthesis as outlined above, since the attacking species can approach either above or below the plane of the ring of compound (I).

Though the process is shown in the reaction chart as proceeding through anionic intermediates, these need not necessarily have an independent existence. The reaction is, however, almost certainly anionic in character, the direction of addition at the first stage being as expected for attack of a nucleophilic reagent on an unsymmetrical fluoro-olefin. If the product (IV) is assumed to arise entirely from (II), then the elimination of fluorine from the $>CHF$ group is about twice as frequent as from $>CF_2$. This presumably is a similar effect to that observed [21,22] in dehydrofluorinations of fluorocyclohexanes. The fluorine in $>CHF$ is less tightly bound than that in $>CF_2$ but, particularly if a *trans*-addition is assumed in the first stage, the stereochemistry may well favour loss of fluorine from the $>CF_2$ group. Neither the penta- (IV) nor the hexa-fluoro-olefin (V) would react further with lithium aluminium hydride under the general conditions used. This must be due to the number of fluorine substituents located around the double bonds—too few to promote nucleophilic attack. It seems, provisionally, that reaction can occur only if four or more fluorine atoms are present on the vinylic and α-carbon atoms.

An alternative route to 1,2,3,4-tetrafluorobenzene was realised starting from the heptafluorocyclohexene (VI) obtained [22,23] by fluorination of benzene with manganic fluoride and, in very small amounts, by the analogous fluorination with cobaltic fluoride.[22] The olefin (VI) was treated with lithium aluminium hydride in dry ether in the usual way and the product contained two new compounds (VII and VIII) which were separated and characterised.



Reagents: 1, AlH_4^-; 2, loss of F^-; 3, KOH.

Compound (VII) was a hexafluorocyclohexene and on oxidation gave a new pentafluoroadipic acid. The presence of $-CH=CF-$, $>CH_2$, and $>CHF$ groups was indicated [18,24]

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[20] Evans, Godsell, Stephens, Tatlow, and Wiseman, *Tetrahedron*, 1958, **2**, 183.
[21] Smith and Tatlow, *J.*, 1957, 2505.
[22] Stephens, Tatlow, and Wiseman, *J.*, 1959, 148.
[23] Fear and Thrower, *J. Appl. Chem.*, 1955, **5**, 353.
[24] Steele and Whiffen, *Tetrahedron*, 1958, **3**, 181.

by infrared absorption peaks at 1710, 2859, and 2949 cm.$^{-1}$, respectively; the last-mentioned frequency is in agreement with disposition of the $>$CHF group α to the double bond. Further, upon dehydrofluorination with aqueous potassium hydroxide, the aqueous phase developed a dark brown colour, as invariably happens when a 1,3-diene is formed. The liquid product of this reaction was shown by gas chromatography to contain two components, with one in large excess. The major component was identified as 1,2,3,4-tetrafluorobenzene, but the other was not obtained in sufficient quantity for identification. Compound (VII) is designated as 1,4,4,5,5,6-hexafluorocyclohexene, from which 1,2,3,4-tetrafluorobenzene would be formed by 1,2-eliminations and a 1,3-diene with two $>CF_2$ groups by a 1,4-elimination.

The second olefin (VIII) was also a hexafluorocyclohexene and on oxidation gave yet a different pentafluoroadipic acid. Its infrared spectrum contained peaks at 1711, 2853, and 2985 cm.$^{-1}$ characteristic of –CH=CF–,[18] $>CH_2$, and $>$CHF groups,[24] respectively, with the last-mentioned typical of one disposed β to the double bond. Dehydrofluorination of this olefin gave only 1,2,3,4-tetrafluorobenzene and the aqueous phase remained colourless. It was significant that the yield of the tetrafluorobenzene was appreciably greater (89%) from this olefin (VIII) than from compound (VII) (56%). The structure (VIII) is thus proved. A reaction scheme analogous to that suggested previously will explain these observations, two products (VII and VIII) being expected because the original attack on the double bond of the unsymmetrical olefin (VI) should proceed in two ways, since only a very weak directional effect would be expected from the β-hydrogen atom. Compound (VII) can give only one stable diene, as indicated, and compound (VIII) cannot give any. A stable diene is one which cannot form an aromatic compound by 1,2- or 1,4-elimination of hydrogen fluoride. A diene is stable if it has two $>CF_2$ groups and presumably should be with two $>CH_2$ groups. However, a cyclohexadiene with both hydrogen and fluorine present on its saturated carbon atoms, is unstable and cannot be isolated from alkaline systems.

Further reaction of the hexafluorocyclohexenes (VII) and (VIII) with lithium aluminium hydride was attempted, to give products with a double bond of the type –CH=CH–. These, on dehydrofluorination, should have given the then unknown 1,2,3-trifluorobenzene, which has since been made by Finger and his co-workers.[13] However, not unexpectedly in view of the earlier results, the double bonds in the cyclohexenes (VII) and (VIII) were not sufficiently activated and no reaction occurred, even with excess of lithium aluminium hydride and prolonged heating.

EXPERIMENTAL

General Techniques.—Unless otherwise stated, oxidations of olefins, gas-chromatographic analyses and separations, and infrared measurements were carried out as described before.[22] Known acids were characterised by two derivatives which had correct elemental analyses in each case reported.

Reaction of 4H/5H-1,3,3,4,5,6,6-*Heptafluorocyclohexene* (I) *with Lithium Aluminium Hydride.*—The cyclohexene (13·0 g.) in diethyl ether (50 c.c.) was added during 30 min. to a stirred suspension of lithium aluminium hydride (2·5 g.) in ether (50 c.c.) at 0°. After a further 2½ hours' stirring at 35°, water (10 c.c.), followed by 8N-sulphuric acid (20 c.c.), was added. The ethereal layer was separated and dried ($MgSO_4$), and most of the solvent was removed by distillation through a 6″ vacuum-jacketed column. The residue, on gas-chromatography, showed four peaks in addition to that due to ether. Separation by preparative-scale gas chromatography (column B, temp. 110°, N_2 flow-rate 48 l./hr.) gave (i) ether, (ii) unchanged heptafluorocyclohexene (1·2 g.), (iii) 4H/5H-3,3,4,5,6,6-*hexafluorocyclohexene* (II) (3·0 g.), b. p. 121—122°, $n_D^{18.5}$ 1·3540 (Found: C, 37·7; H, 2·1; F, 60·0. $C_6H_4F_6$ requires C, 37·9; H, 2·1; F, 60·0%), (iv) 5*H*,6*H*-1,4,4,5,6-*pentafluorocyclohexene* (IV) (1·0 g.), b. p. 127—128°, $n_D^{16.5}$ 1·3748 (Found: C, 41·9; H, 2·9. $C_6H_5F_5$ requires C, 41·9; H, 2·9%), and (v) mixed 5*H*,6*H*-1,3,4,4,5,6-hexafluorocyclohexenes (V) (1·9 g.), b. p. 133—134°, n_D^{20} 1·3684 (Found: C, 37·9; H, 2·2%).

Characterisation of 4H/5H-3,3,4,5,6,6-*Hexafluorocyclohexene* (II).—(*a*) The hexafluorocyclohexene (0·5 g.), potassium permanganate (1·6 g.), and dry acetone (40 c.c.) gave (±)-3*H*,4*H*-hexafluoroadipic acid [12] (69%).

(*b*) The olefin showed a characteristically very weak absorption at 1700 cm.$^{-1}$ for a –CH=CH– group; [18] this spectrum was identical with that of the hexafluorocyclohexene isolated from the product of the partial fluorination of benzene.[22] Also there was no selective ultraviolet absorption over the range 2400—3000 Å.

(*c*) The hexafluorocyclohexene (2·3 g.), potassium hydroxide (5·0 g.), and water (5 c.c.) were shaken together in a sealed tube at 100° for 3 hr. The liquid product (1·1 g.) was shown by gas chromatography to contain two components which were separated by gas chromatography (column A, temp. 110°, N_2 flow-rate 10·6 l./hr) to give 1,3,3,6,6-*pentafluorocyclohexa*-1,4-*diene* (III) (0·2 g.), n_D^{22} 1·3520 (Found: C, 42·4; H, 1·6. $C_6H_3F_5$ requires C, 42·4; H, 1·8%), and 1,2,3,4-tetrafluorobenzene (0·7 g.), b. p. 93—94°, n_D^{20} 1·4054 (Found: C, 48·2; H, 1·5. Calc. for $C_6H_2F_4$: C, 48·0; H, 1·3%), for which Pummer *et al.*[14] gave b. p. 94·8—95°.

Characterisation of 1,3,3,6,6-*Pentafluorocyclohexa*-1,4-*diene*.—The diene (0·4 g.), potassium permanganate (2·0 g.), and dry acetone (500 c.c.) gave difluoromalonic acid (39%).

The diene showed two main infrared bands, at 1676 and 1729 cm.$^{-1}$.[18] There was no selective ultraviolet absorption in the range 2400—3000 Å.

Characterisation of 1,2,3,4-*Tetrafluorobenzene*.—(i) *Sulphonation*. The tetrafluorobenzene (1·3 g.) and stabilised sulphur trioxide (6·0 g.) were kept in a sealed vessel at 15° for 22 hr. Then concentrated sulphuric acid (10 c.c.) was added and the solution poured on ice and continuously extracted with ether for 48 hr. The ether solution was washed with water, dried ($MgSO_4$), filtered, and evaporated to leave a white solid (1·5 g.) which, on sublimation at 100°/0·05 mm., gave the very hygroscopic 2,3,4,5-*tetrafluorobenzenesulphonic acid*, m. p. 73—74° (Found: equiv., 232. $C_6H_2F_4O_3S$ requires equiv., 230). S-*Benzylthiouronium* 2,3,4,5-*tetrafluorobenzenesulphonate* had m. p. 188° (from water) (Found: C, 42·6; H, 3·0. $C_{14}H_{12}F_4N_2O_3S_2$ requires C, 42·4; H, 3·0%).

(ii) *Bromination*. The tetrafluorobenzene (2·2 g.) was added to a stirred mixture of bromine (6·0 g.), fuming sulphuric acid (20% SO_3; 8 c.c.), and aluminium bromide (0·1 g.). After 10 hr. at 60—65° the bromination mixture was poured on ice (200 g.), the organic layer extracted with ether, and the extract washed with sodium carbonate solution, sodium metabisulphite solution, and water. The ethereal solution was dried ($MgSO_4$) and evaporated, to leave a liquid residue which was distilled to give 1,2-*dibromo*-3,4,5,6-*tetrafluorobenzene* (1·7 g.), b. p. 194—195°, n_D^{18} 1·5064, $\lambda_{max.}$ 2510 and 2700 Å (ε 1196 and 1022, respectively; *c* 0·19 in EtOH) (Found: C, 23·8; F, 24·8. $C_6Br_2F_4$ requires C, 23·4; F, 24·7%).

(iii) *Spectroscopy*. A strong infrared band was displayed at 1525 cm.$^{-1}$, characteristic of an aromatic ring; the spectrum was different from those of 1,3,4,5- and 1,2,4,5-tetrafluorobenzene, but identical with that of 1,2,3,4-tetrafluorobenzene supplied by Dr. Wall. A band was shown in the ultraviolet spectrum with $\lambda_{max.}$ 2600 Å (ε 649; 0·19 in EtOH).

Characterisation of 5*H*,6*H*-1,4,4,5,6-*Pentafluorocyclohexene*. (IV)—(*a*) The pentafluorocyclohexene (1·5 g.) potassium permanganate (4·5 g.), and dry acetone (600 c.c.) were shaken together for 6 hr. Water (200 c.c.) was then added and the acetone removed at diminished pressure. The acid, isolated as above (1·4 g.) and twice sublimed at *ca.* 160°/0·1 mm., was αββ′β′-*tetrafluoroadipic acid*, m. p. 172—173° (Found: C, 33·0; H, 2·8%; equiv., 220. $C_6H_6F_4O_4$ requires C, 33·0; H, 2·75%; equiv., 218). A portion of the acid (0·2 g.) was dissolved in water (3 c.c.), the pH was adjusted to 4 with 2N-sodium hydroxide, and a saturated solution of *S*-benzylthiouronium chloride was added. The precipitate recrystallised from water, to give *di*-(S-*benzylthiouronium*) αββ′β′-*tetrafluoroadipate* (0·5 g.), m. p. 182° (Found: C, 47·8; H, 4·6. $C_{22}H_{26}F_4N_4O_4S_2$ requires C, 48·0; H, 4·7%). The acid formed an unstable anilinium salt.

(*b*) The cyclohexene showed an absorption band at 1710 cm.$^{-1}$ characteristic of a –CH=CF– group.[18]

(*c*) The cyclohexene (3·9 g.), potassium hydroxide (8·0 g.), and water (8 c.c.) were shaken together in a sealed tube at 100° for 2 hr. A portion (1·9 g.) of the liquid product (2·2 g.) was separated by gas chromatography (column A, temp. 100°, N_2 flow-rate 10·1 l./hr.) to give 1,2,4-trifluorobenzene (1·3 g.), n_D^{20} 1·4218 (Found: C, 54·6; H, 1·9. Calc. for $C_6H_3F_3$: C, 54·5; H, 2·25%), whose infrared absorption was identical with that of an authentic specimen over the range 3000—700 cm.$^{-1}$.

Characterisation of the Mixed 5*H*,6*H*-1,3,4,4,5,6-*Hexafluorocyclohexenes* (V).—(*a*) The hexafluorocyclohexenes (0·5 g.) were oxidised with potassium permanganate (2·3 g.) in dry acetone

(200 c.c.) as previously described. The free acid was not isolated but was converted directly into a *di-(S-benzylthiouronium) pentafluoroadipate* (0·4 g.), m. p. 195—196° (Found: C, 46·3; H, 4·1. $C_{22}H_{25}F_5N_4O_4S_2$ requires C, 46·5; H, 4·4%). The dianilinium salt appeared to be unstable.

(*b*) The specimen showed an absorption band at 1710 cm.$^{-1}$, characteristic of a –CH=CF– group.[18]

(*c*) The cyclohexenes (3·3 g.), potassium hydroxide (6·6 g.), and water (7 c.c.) were heated in a sealed tube at 100° for 2 hr. with continuous shaking. The liquid product (2·0 g.) was shown to contain three components by gas chromatography; these were separated on a preparative-scale column (A, temp. 100°, N_2 flow-rate 10 l./hr.) to give 1,2,3,5-tetrafluorobenzene (0·3 g.), n_D^{20} 1·4006, 1,2,4,5-tetrafluorobenzene (0·5 g.), n_D^{20} 1·4048, and 1,2,3,4-tetrafluorobenzene (0·3 g.). The infrared spectrum of each tetrafluorobenzene was identical with that given by the appropriate authentic specimen.

(*d*) The mixed cyclohexenes (2·9 g.) were passed in a stream of nitrogen (5 l./hr.) through a copper tube (13″ × ¼″ external diameter) heated to 70° and packed with cobaltic fluoride (*ca.* 7 g.) supported on nickel gauze cylinders (1/16″ × 1/16″). The addition was complete in 20 min. and the solid product, collected in a glass trap cooled by liquid oxygen, was dissolved in ether. The ethereal solution was separated by vapour-phase chromatography (column A, temp. 104°, N_2 flow-rate 10 l./hr.) into three main fractions, which were identified by gas chromatography and infrared spectroscopy. The first fraction (0·3 g.) was 1*H*,4*H*/2*H*-nonafluorocyclohexane, the second (0·45 g.) a mixture of approximately equal amounts of 1*H*/2*H*,4*H*-nona- and 1*H*,4*H*/2*H*,5*H*-octa-fluorocyclohexane, and the last fractions (0·27 g.) a $\sim$4 : 1 mixture of 1*H*,2*H*,4*H*/5*H*- and 1*H*,5*H*/2*H*,4*H*-octafluorocyclohexane.

Reaction of 4H/5H-3,3,4,5,6,6-*Hexafluorocyclohexene with Lithium Aluminium Hydride.*—The hexafluorocyclohexene (1·0 g.) in diethyl ether (10 c.c.) was added dropwise to a stirred suspension of lithium aluminium hydride (0·25 g.) in dry ether (20 c.c.), and the mixture was refluxed for 3 hr. Then water (5 c.c.) was added, followed by sufficient 50% sulphuric acid to dissolve the precipitate. The ether solution was separated and dried ($MgSO_4$) and the main part of the solvent removed by distillation. Gas-phase chromatography of the residue gave two peaks, in addition to that of ether, with retention times identical with those of the unchanged hexafluorocyclohexene and of 5*H*,6*H*-1,4,4,5,6-pentafluorocyclohexene as established by enrichment of the mixture with authentic specimens. The infrared absorption spectrum of the reaction mixture over the range 3000—750 cm.$^{-1}$ was consistent with the presence of these two compounds and no others.

Reaction of 3,3,4,4,5,6,6-*Heptafluorocyclohexene* (VI) *with Lithium Aluminium Hydride.*—The cyclohexene [22, 23] (13·0 g.) in dry ether (50 c.c.) was added during 5 min. to a stirred suspension of lithium aluminium hydride (2·5 g.) in dry ether (150 c.c.) at 20°. The whole was stirred for a further 4 hr. at *ca.* 35°, then water (25 c.c.), followed by 15N-sulphuric acid (20 c.c.), was added. The ether layer was separated, dried ($MgSO_4$), and filtered and the main part of the solvent was removed through a 6″ vacuum-jacketed column packed with nickel Dixon gauze rings (1/16″ × 1/16″). The residue was shown by gas chromatography to contain two components in addition to ether. Separation by gas chromatography (column B, temp. 110°, N_2 flow-rate 48 l./hr.) gave (i) ether, (ii) 1,4,4,5,5,6- (VII) (3·0 g.), b. p. 119—120°, n_D^{18} 1·3540 (Found: C, 37·8; H, 2·4. $C_6H_4F_6$ requires C, 37·9; H, 2·1%), and (iii) 1,4,4,5,6,6-*hexafluorocyclohexene* (VIII) (5·6 g.), b. p. 120—121°, n_D^{18} 1·3554 (Found: C, 38·0; H, 2·3%).

Characterisation of 1,4,4,5,5,6-*Hexafluorocyclohexene* (VII).—(*a*) The hexafluorocyclohexene (0·5 g.), potassium permanganate (0·8 g.), and dry acetone (100 c.c.) were shaken together at 18° for 1 hr. Water (50 c.c.) was then added and the mixture shaken for 10 min. The acetone was then removed and the isolation of the acid followed the usual procedure. The crude acid was dissolved in water, the pH adjusted to 4, and *S*-benzylthiouronium chloride added to give *di-(S-benzylthiouronium) αββ′β′-pentafluoroadipate* (0·6 g.), m. p. 183° (decomp.) (Found: C, 46·7; H, 4·7. $C_{22}H_{25}F_5N_4O_4S_2$ requires C, 46·5; H, 4·4%).

(*b*) Absorption maxima were at 1710, 2859, and 2949 cm.$^{-1}$.

(*c*) The hexafluorocyclohexene (2·0 g.), potassium hydroxide (4·0 g.), and water (4 c.c.) were shaken together in a sealed tube at 100° for 2 hr. The pale-brown aqueous phase was separated from the hydrofluorocarbon (0·85 g.) which was shown by gas chromatography to contain, in addition to the unchanged hexafluorocyclohexene, 1,2,3,4-tetrafluorobenzene (infrared spectrum) and a very minor component, with slightly shorter retention time.

Characterisation of 1,4,4,5,6,6-*Hexafluorocyclohexene* (VIII).—(*a*) The hexafluorocyclohexene

(0·5 g.) was oxidised with potassium permanganate (0·8 g.) in dry acetone (100 c.c.) as described for the previous oxidation and the fluoro-acid isolated in the same way. The dianilinium salt appeared unstable and the acid was characterised as *di-*(S-*benzylthiouronium*) ααββ′β′-*pentafluoroadipate* (0·7 g.), m. p. 187° (Found: C, 46·7; H, 4·4%).

(*b*) Absorption bands were at 1711, 2853, and *ca.* 2985 cm.$^{-1}$.

(*c*) The cyclohexene (2·5 g.) was dehydrofluorinated with potassium hydroxide (5·0 g.) in water (5 c.c.) as described for its isomer. The colourless aqueous layer was separated from the hydrofluorocarbon (1·7 g.) which was shown by gas chromatography and infrared spectroscopy to be pure 1,2,3,4-tetrafluorobenzene.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

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