Reactions of 3,3,4,4-Tetrafluorohexa-1,5-diene. Part II.† Cyclisation to a Four-membered Ring in the Thermal Addition of Pentafluoroiodoethane

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Pentafluoroiodoethane reacts at 210-220° with 3,3,4,4-tetrafluorohexa-1,5-diene to give unusual cyclisation products having a four-membered ring, contrary to analogous reactions of perfluoroalkyl iodides with hexa-1,5diene and in spite of the unfavourable entropy change to give highly strained ring structure. Also minor amounts of an isomeric saturated monoadduct containing a five-membered ring and of acyclic monoadduct were isolated. The structures of the cyclic products were elucidated by spectroscopic and chemical methods.

CYCLIC polymerisation of hexa-1,5-diene to give saturated polymeric chains containing five-membered ring units has been reported.¹ The free-radical chain reaction of hexa-1.5-diene with heptafluoro-1-iodopropane gives² only the olefinic and saturated acyclic adducts as a result of the addition of one or two R_FI molecules, respectively, confirming the poor overlap of the orbitals between a radical and a $\gamma\delta$ -double bond.

We report here the thermally induced addition at 200-220 °C, of pentafluoroiodoethane to 3,3,4,4-tetrafluorohexa-1,5-diene (I), which yields a large amount of a mixture of isomeric saturated monoadducts besides a minor proportion of the acyclic monoadduct (II) and the transformation product (III) of the linear diadduct.

$$CH_{2}:CH \cdot [CF_{2}]_{2} \cdot CH:CH_{2} \quad (I)$$

$$CF_{3} \cdot CF_{2} \cdot CH_{2} \cdot CHI \cdot [CF_{2}]_{2} \cdot CH:CH_{2} \quad (II)$$

$$CF_{3} \cdot CF_{2} \cdot [CH_{2}]_{2} \cdot [CF_{2}]_{2} \cdot CH:CH \cdot CF_{2} \cdot CF_{3} \quad (III)$$

The saturated monoadduct fraction is a mixture of two isomers containing a CH₂I group and a smaller amount of a compound containing a CHI group. It seems possible that the intermediate radical, formed by initial attack of the thermally generated pentafluoroethyl radical on the CH, group of compound (I), might cyclise to a five-membered ring and give by transfer with CF₃·CF₂I one of two isomers of the cyclopentane adduct (IV). The compound with the CH₂I group might contain a four- or a five-membered ring. The latter would readily be formed via an 'anti-Kharasch' addition to the terminal double bond of (I) to give a substituted hex-5-enyl radical. Radicals of this type

$$R \cdot CH \cdot [CF_2]_2 \cdot CH : CH_2$$
 (R = CF₃ · CF₂ · CH₂)



are known³ to give cyclopentane derivatives easily and preferentially. Surprisingly n.m.r. spectroscopy has shown that the products containing the CH₂I group are cis- and trans-isomers of a strained 4 four-

$$CH_{2}:CH \cdot [CF_{2}]_{2} \cdot CHR' \cdot \dot{C}H_{2} \longrightarrow H \xrightarrow{R' + H_{2} + CH_{2}} H \xrightarrow{F_{2} + F_{2}} H$$

$$(R'_{2} CF_{3} \cdot CF_{2})$$

membered ring derivative, 3,3,4,4-tetrafluoro-1-iodomethyl-2-(2,2,3,3,3-pentafluoropropyl)cyclobutane (V).

³ R. C. Lamb, P. W. Ayers, and M. K. Toney, J. Amer. Chem. Soc., 1963, 85, 3483. ⁴ W. A. Bernett, J. Org. Chem., 1969, 84, 1772.

[†] Part I, P. Piccardi, M. Modena, and E. Santoro, J. Chem. Soc. (C). 1971, 3894.

¹ H. S. Makowski, B. K. C. Shim, and Z. W. Wilchinsky, J. Polymer Sci., Part A-1, Polymer Chem. 1964, 2, 1549.
 ² N. O. Brace, J. Org. Chem., 1966, 31, 2879.

The proton spectra (Table 3) fail to show the resonance of the CH₂ group at high field (τ ca. 8.0–8.5) characteristic of the cyclopentane ring. In addition in both proton and fluorine spectra there is evidence of H-F vicinal coupling (J 16-19 Hz) in the system CH₂·CF₂ present only in structure (V). We were also able to measure the geminal F-F coupling constant of the difluoromethylene groups in the ring system. Data from the literature and from our unpublished results support the hypothesis that this coupling changes systematically from 150-200 Hz in the cyclopropane⁵ series to 190-230 Hz in cyclobutanes,⁶ 230-260 Hz in cyclopentanes,7 and 270-300 Hz in cyclohexanes.8 In our case the experimentally observed values range between 212 and 216 Hz which is a further indication of the four-membered ring structure. The five-membered ring structure ascribed to compound (IV) has to be preferred to that with a six-membered ring, for reasons similar to those given for the preceding cyclobutane compounds, that is to say, the lack of a strong proton resonance corresponding to four protons at high field $(\tau \ ca. \ 8.0)$ and the value of the geminal F-F coupling constant (ca. 240 Hz) characteristic of a fluorinated cyclopentane. Additional evidence for structure (V) has been obtained from the isomerisation of compound (II). Treatment of compound (II) with di-t-butyl peroxide as initiator at 120° in cyclohexane solution caused isomerisation to trans- and cis-2,2,3,3-tetrafluoro-1-iodomethyl-4-(2,2,3,3,3-pentafluoropropyl)-

cyclobutane (V). The cyclisation of (II) by a free-

$$R = CF_3 \cdot CF_2 \cdot CH_2$$

$$R = CF_3 \cdot CF_2 \cdot CH_2$$

radical process evidently takes place through the same intermediate radical as generated by thermally induced addition of perfluoroiodoethane to (I). However under these conditions no evidence of the isomeric fivemembered compound (IV) was obtained. The presence of a CH_2I group in (V) was easily proved, following the procedure employed by Brace,² by reduction of the cyclic adduct mixture with zinc and hydriodic acid to *cis*- and *trans*-isomers of the methylcyclobutane derivative (VI). Dehydroiodination of (V) with potassium hydroxide gave one methylenecyclobutane derivative (VII) which adds hydrogen to give both isomers of (VI).

The n.m.r. spectra of compound (VII) (Table 3) do not show any resonance that could be attributed to a CH_2 group in a five-membered ring. Indeed a signal at $\tau 6.43$ (intensity one) can be interpreted as arising from a CH group near to an sp^2 carbon atom, in

agreement with structure (VII). When the dehydroiodination was carried out by slowly dropping compound (V) into an ethylene glycol solution of an excess of



potassium hydroxide, kept at $140-145^{\circ}$, and continuously distilling off the reaction products as soon as they were formed, besides (VII), other products of



successive dehydrofluorination and of reactions with glycol were isolated. These compounds might be formed

⁸ K. W. Jolley, L. H. Sutcliffe, and S. M. Walker, *Trans. Faraday Soc.*, 1968, **64**, 269, and references cited therein.

⁵ R. A. Mitsch, J. Amer. Chem. Soc., 1965, 87, 758; P. B. Sargeant, J. Org. Chem., 1970, 35, 578; L. Cavalli, Org. Magnetic Resonance, 1970, 2, 233, and references cited therein.

 ⁶ W. D. Phillips, J. Chem. Phys., 1956, 5, 949; R. R. Ernst, Mol. Phys., 1969, 16, 241, and references cited therein.

⁷ R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G. Orrell, *J. Chem. Soc.* (C), 1967, 1608; R. E. Banks, M. G. Barlow, R. N. Haszeldine, M. Lappin, V. Matthews, and N. I. Tucker, *ibid.*, 1968, 548; P. B. Sargeant, *J. Amer. Chem. Soc.*, 1969, **91**, 3061.

as shown in Scheme 1. For (VIII) a possible structure of type (A) was rejected only on the basis of the HF

CF3.CF CH3 (A)

coupling constant. The value of this coupling (34 Hz) can only derive from a trans-interaction through a double bond.9 We performed some double resonance experiments, irradiating at the CF₃ frequency while observing the vinylic fluorine resonance. In this way we could show a coupling constant (12.8 Hz) coming from an equivalent ring CF₂ group in the d position (see Table 3). Even if the interacting nuclei are separated by five bonds, the coupling has a high value which can be justified by a 'through-space' mechanism.¹⁰ It is known that this interaction can operate whenever the geometry of the molecule favours the proximity of the interacting nuclei. The n.m.r. spectrum of (IX) shows the same resonance as (VIII), together with that of the missing CF₂. The lack of the coupling constant (J 12.8 Hz) that is found in (VIII) between the vinylic fluorine and a difluoromethylene group in the ring system, is clear evidence that the ethylene acetal group is in the position shown.

The effect of the reaction conditions on the relative amounts of the cyclisation and open-chain products has not been determined.

The mixture of compound (IV) and the cis- and transisomers (V) could not be separated by fractional distillation, but was achieved by g.l.c., which was also used to determine the composition of the product mixture. An attempt to reduce compound (IV) by treatment of a distillation fraction containing (IV) as the main product with zinc was unsuccessful; the reaction gave an olefinic product (X) by deiodofluorination. Attempted reduction of (IV) by lithium aluminium hydride also gave compound (X).



The formation of (III) was not unexpected since, in general, addition of polyfluoroalkyl iodides to hydrogenated olefins gives heat-sensitive products, so dehydroiodination occurs readily leading to olefinic products and HI, which may then reduce the iodinecontaining adduct. In contrast, the appreciable yield of (III) and the absence of linear diadduct or its monodehydroiodinated product, even when the reaction was carried out in the presence of an aliphatic ester,¹¹ were surprising. Compound (III) may be formed by intramolecular transfer of hydrogen and elimination of iodine from the radical (B). On the other hand the poor yields of 3,3,4,4,7,7,8,8,8-nonafluoro-oct-1-ene (XI),



the traces of (VI), and the absence of 3,3,4,4,7,7,8,8,8nonafluoro-octa-1,5-diene (XII) show that a limited amount of HI is present. Compound (II) was readily dehydroiodinated by bases, and some reactions of the linear products (II), (III), and (XI) are shown in Scheme 2.



Significant amounts of other, unidentified compounds were present in the products. A detailed study of the distribution of these high-boiling compounds was not made since these could not be readily separated by distillation or by g.l.c. It appears however that the saturated cyclic 1:2 adduct is the main component, with a little of an iodine-free compound of molecular weight 546 (probably derived from the coupling of two cyclic radicals). The former compound was shown by n.m.r. to contain a CH₂I group and was converted by zinc reduction into a derivative containing a methyl group.

EXPERIMENTAL

Products were identified by elemental analysis, molecular weight determination (Mechrolab vapour pressure osmometer model 301A), i.r. spectroscopy (Perkin-Elmer 225 grating spectrophotometer), ¹H and ¹⁹F n.m.r. spectroscopy (Varian HA 100 spectrometer; the data in Table 3 were recorded with tetramethylsilane and trichlorofluoromethane as internal references at 100 and 94.1 MHz, respectively), and mass spectrometry ¹² (Hitachi-Perkin-Elmer RMU/6E instrument). Analytical g.l.c. was carried out with a column $(4 \text{ m} \times 4 \text{ mm})$ packed with tricresyl phosphate (20%) on 60-80 mesh Celite or a column (4 $m \times 4$ mm) packed with Apiezon L on Chromosorb: temperatures were 40-150°.

¹⁰ R. Fields, M. Green, and A. Jones, J. Chem. Soc. (B), 1967, 270, and references cited therein; K. L. Servis and K. N. Fang, J. Amer. Chem. Soc., 1968, 90, 6712.
 ¹¹ N. O. Brace, U.S.P. 3,016,406/1962.
 ¹² S. Saratara en and the destruction of the second sec

⁹ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' vol. 2, Pergamon, Oxford, 1966, p. 911.

¹² E. Santoro, unpublished results.

J. Chem. Soc. (C), 1971

Thermal Addition of Pentafluoroiodoethane to 3,3,4,4-Tetrafluorohexa-1,5-diene (I).—The results of a set of experiments all carried out by the same procedure are collected in Table 1. Compound (I) (92·2 g, 598·2 mmol) was placed in a stainless steel rocking autoclave (400 ml), which was then closed, cooled to -80° , and evacuated, so that pentafluoroiodoethane (224·3 g, 912·1 mmol) could be distilled *in vacuo* into it. The autoclave was heated str.), m/e 400 ($C_8H_6F_9I^+$, 33%), 253 ($C_8H_5F_8^+$, 15%), 209 ($C_6H_4F_7^+$, 12%), 127 (I^+ , $C_4H_3F_4^+$, 10%), 95 ($C_3H_2F_3^+$, 15%), 77 ($C_3H_3F_2^+$, 100%), 69 (CF_3^+ , 12%), 51 (CHF_2^+ , 38%), and 27 ($C_2H_3^+$, 10%). Careful refractionation of fraction 8 was unsuccessful in separating isomers of 3,3,4,4tetrafluoro-1-iodomethyl-2-(2,2,3,3-pentafluoropropyl)cyclobutane (V) (Found: C, 24.0; H, 1.6. $C_8H_6F_9I$ requires C, 24.0; H, 1.5%), b.p. 101° at 50 mmHg [*cis*

TABLE 1

Thermal additions

Reactants		-	con-		Molar composition of the recovered product $(\%)$								
C ₂ F ₅ I	(1)	7100	Time	version	TID	(111)	(117)		X	(VI)	(NTT)	(D) +	(0) T
(mmol)	(mmoi)	I/C	(п)	(%)	(11)	(111)	(1)	<i>cis</i> -(v)	trans-(v)	(AI)	(AII)	(\mathbf{P})	(Q) ‡
912.1	598.2	220	9	74.1	8.0	22.7	5.5	$35 \cdot 6$	11.8	$2 \cdot 6$	0.1	12.6	1.1
923.0	$648 \cdot 8$	210 - 220	4	55.4	25.5	$13 \cdot 4$	$7 \cdot 2$	$29 \cdot 2$	10.7			14.0	
988.9	648.8	210 - 220	9	71.9	10.5	20.2	6.9	32.6	10.5	Trace		16.5	2.8
406·2 *	266.7	210	5	$43 \cdot 2$	13.1	9.5	8.5	$34 \cdot 6$	14·3	1.1		18.0	
						1.1. /10 -	1) + -	C1:- 1 -	0.33.477	5 P P A	+ 0		

* Reaction carried out in the presence of ethyl acetate (40 ml). \dagger Cyclic 1:2 adduct (M 554). \ddagger Compound of M 546 (see text).

at 220° and rocked for 9 h. The volatile products (91.7 g) were removed by heating (70°) and pumping through a cold (-190°) trap. A solution of the slushy residue

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Frac- tion	Vapour temp. (°C)	Pres- sure (mmHg)	Amount collected	G.l.c. analysis (approximate wt %)
10.		(111116)	(6)	() E I
1	10.9-11.9	155	09.1	C ₂ F ₅ I
2	31 - 41	755	13.1	$C_{2}F_{5}I$ (45); Et ₂ O (55)
3	38 - 39	100	$3 \cdot 1$	(XII) (2): (I) (46):
	00 00		• -	(XI) (44); (III) (8)
4	58-65	100	1.8	(XI) (80); (III) (20)
5	82 - 83	100	34.3	(III)
6	104 - 105	100	10.8	(II)
7	112-119	100	3.3	(II) (52); (V) (cis-, 37;
				trans-, 11)
8	120 - 124	100	79.2	(V) (cis-, 69; trans-,
				(1V) (9)
9	60 - 62	10	$2 \cdot 4$	trans- (V) (34); (IV)
				(66)
10	105 - 107	5	$2 \cdot 4$. ,
m			90.1	
Residue			29.1	

(219.0 g) in diethyl ether was washed with aqueous sodium thiosulphate and dried (MgSO₄). Ether was removed under reduced pressure and the residue $(184 \cdot 2 \text{ g})$ was added to the volatile products and distilled. The results of the distillation are shown in Table 2. 3,3,4,4,7,7,8,8,8-Nonafluoro-oct-1-ene (XI) was separated by g.l.c. from fraction 4 (Found: C, 35.2; H, 2.3. C8H7F9 requires C, 35.05; H, 2.55%), b.p. 112-112.5° at 755 mmHg (microdetermination); λ_{max} , 6.06 µm (C:C str.); m/e 274 (C₈H₇F₉⁺, 2.5%), 197 (C₅H₄F₇⁺, 9%), 177 (C₅H₃F₆⁺, 7%), 77 (C₃H₃F₂⁺, 100%), and 51 (CHF₂⁺, 47%). Redistillation of fraction 5 gave 1,1,1,2,2,5,5,6,6,9,9,10,10,10-tetradecafluorodec-3-ene (III) (Found: C, 30.7; H, 1.7%; M, 392. $C_{10}H_{6}F_{14}$ requires C, 30.65; H, 1.55%; M, 392.2), b.p. 141.4— 141.8° at 755 mmHg; m/e 392 ($C_{10}H_6F_{14}^+$, 41%), 197 ($C_5H_4F_7^+$, 100%), 195 ($C_5H_2F_7^+$, 50%), 177 ($C_5H_3F_6^+$, $(C_{4}H_{3}F_{4}^{+}, 35\%), 113 (C_{3}HF_{4}^{+}, 30\%), 77$ $(C_{3}H_{3}F_{2}^{+}, 23\%)$, 69 $(CF_{3}^{+}, 26\%)$, and 51 $(CHF_{2}^{+}, 26\%)$. Fraction 6 gave 3,3,4,4,7,7,8,8,8-nonafluoro-5-iodo-oct-1-ene (II) (Found: C, 24.0; H, 1.7%; M, 400. C₈H₆F₉I requires C, 24.0; H, 1.5%; M, 400.0), b.p. 171-172° at 755 mmHg (microdetermination); λ_{max} 6.06 µm (C:C

79%; trans 21% (by g.l.c.)], m/e 400 (C₈H₆F₉I⁺, 28%), 253 $(C_8H_5F_8^+, 32\%)$, 209 $(C_6H_4F_7^+, 26\%)$, 77 $(C_3H_3F_2^+, 26\%)$ 100%), 69 (CF_3^+ , 13%), and 51 (CHF_2^+ , 27%). A sample of a single isomer of 2,2,3,3-tetrafluoro-1-iodo-4-(2,2,3,3,3pentafluoropropyl)cyclopentane (IV) was trapped by g.l.c. from fraction 9, m/e 400 (C₈H₈F₉I⁺, 54%), 253 (C₈H₅F₈⁺, 44%), 209 (C₆H₄F₇⁺, 34%), 77 (C₃H₃F₂⁺, 100%), 69 (CF₃⁺, 100%), 69 (CF₃⁺), 100%), 69 (CF₃⁺, 100%), 69 (CF₃⁺), 100%), 69 (CF₃⁺), 100%), 100%), 100% 18%), and 51 (CHF₂⁺, 31%). The mass spectrum of fraction 10 [Found: M, 546 (osmometry). C₁₆H₁₂F₁₈ requires M, 546.3] was consistent with the presence of one compound having a parent ion at m/e 546 and a minor amount of the 1:2 adduct; the n.m.r. spectrum showed no vinylic proton resonance. The solid residue was dissolved in boiling carbon tetrachloride; on cooling the 1:2 adduct separated (27.5 g, 49.6 mmol) (Found: C, 30.5; H, 2.2; I, 22.8%; M, 554. C14H12F13I requires C, 30·35; H, 2·2; I, 22·9%; M, 554·2), m.p. 154°. The n.m.r. spectrum (in [2H6] acetone) showed no olefinic proton resonances; the CH_2I resonance appeared at τ 6.75. Reduction with zinc was performed as for compound (V) (see later) to give the methyl compound (Found: C, 39.3; H, 3.1. C₁₄H₁₃F₁₃ requires C, 39.25; H, 3.05%), m.p. 92—93° (from carbon tetrachloride), τ 8.8 (Me).

Dehydroiodination of cis- and trans-Isomers of (V).-A mixture of cis- (72%) and trans- (28%) isomers of (V) (61.0 g, 152 mmol) was added (3 h) under nitrogen to a stirred solution of potassium hydroxide (20 g, 356 mmol) in ethylene glycol (150 ml) at 130-135°; the products were continuously distilled off during the addition. After being washed with water and dried (MgSO₄), the products (24.2 g) were fractionated, giving (i) 3,3,4,4-tetrafluoro-1-methylene-2-(2,2,3,3,3-pentafluoropropyl)cyclobutane (VII) (17 g, 62 mmol, 41%), m/e 272 (C₈H₅F₉⁺, 5%), 203 (C₇H₅F₆⁺, 44%), 153 ($C_6H_5F_4^+$, 48%), 139 ($C_5H_3F_4^+$, 47%), 77 $(C_3H_3F_2^+, 53\%), 76 (C_3H_2F_2^+, 100\%), 75 (C_3HF_2, 33\%),$ 69 (CF_3^+ , 29%), and 51 (CHF_2^+ , 26%) (Found: C, 35.2; H, 1.9. C₈H₅F₉ requires C, 35.3; H, 1.85%), b.p. 117° at 755 mmHg, λ_{max} 5.98 µm (C:C str.), (ii) a fraction (3.1 g), b.p. 118—119°, and (iii) a residue (6.6 g). G.l.c. of fraction (ii) gave compound (VII) (31%), and 3,3,4,4-tetrafluoro-1-methyl-2-(2,3,3,3-tetrafluoroprop-1-enyl)cyclobutene (VIII) (69%), λ_{max} . 5.85 (CF:CH str.) and 6.08 μ m (C:C str.). Fraction (iii) was shown by g.l.c. to contain starting material (V) (3.8 g, 9 mmol) and 4,4-*difluoro*-3-*methyl*-2-(2,3,3,3-*tetrafluoroprop*-1-*enyl*)*cyclobut*-2-*en*-1-*one ethylene acetal* (IX) (2.8 g, 10 mmol, 7%) (Found: C, 43.9; H, 3.0. C₁₀H₈F₆O₂ requires C, 43.8; H, 2.95%), m.p. 68—69° (from diethyl ether); λ_{max} 5.88 (CF:CH str.) and 6.09 µm (C:C str.), *m/e* 274 (C₁₀H₈F₆O₂⁺, 97%), 205 (C₉H₈F₃-O₂⁺, 44%), 133 (C₆H₄F₃⁺, 100%), and 28 (C₂H₄⁺, CO⁺, 38%).

Zinc Reduction of Compound (V) .--- To a well stirred mixture of compound (V) [cis (33.9 g, 84.7 mmol), trans (16 g, 40.6 mmol)], ethanol (200 ml), and zinc dust (20-40 mesh; 28 g, 0.428 g atom) aqueous 57% hydriodic acid (60 ml) was added at 72-74°, under reflux. A further 10 ml of hydriodic acid was added after 1.5 h. After 2 h the liquid was decanted into a separating funnel and water (100 ml) was added. The organic layer was separated, washed with sodium hydrogen carbonate solution and water, and dried (MgSO₄). The product (32.1 g) was fractionally distilled to give, besides starting material (1.7 g, 4.8 mmol) as residue, a fraction (28.4 g, 103.5 mmol, 82.5%) shown by g.l.c. to be a mixture of *cis*- (68\%) and trans- (32%) isomers of 3,3,4,4-tetrafluoro-1-methyl-2-(2,2,3,3,3-pentafluoropropyl)cyclobutane (VI), m/e274 (C_8H_7F_9^+, 0.5%), 78 (C_8H_4F_2^+, 100\%), and 77 (C_3H_3F_2^+, 28%). The isomers were separated by g.l.c. to give cis-(VI) (Found: C, 35.2; H, 2.8. C₈H₇F₉ requires C, 35.05; H, 2.55%), b.p. 118.1-118.6° at 755 mmHg, and trans-(VI) (Found: C, 35.1; H, 2.9%), b.p. 124-125° at 755 mmHg.

Zinc Reduction of a Mixture of Compounds (IV) and (V).-To a well stirred mixture of (IV) (11.1 g, 27.7 mmol) and trans-(V) (12.8 g, 32.0 mmol), ethanol (200 ml), and zinc (20-40 mesh, 15.6 g, 0.239 g atom), aqueous 57% hydriodic acid (32 ml) was added at $72-74^{\circ}$, under reflux. After 2.5 h the liquid was decanted into water (200 ml) and the organic layer was separated, washed with sodium hydrogen carbonate solution, and dried (MgSO₄). The product (14.6)g) was distilled, giving trans-(VI) (8.2 g, 29.9 mmol, 93%) 1,5,5-trifluoro-4-(2,2,3,3,3-pentafluoropropyl)cyclopentand ene (X) (5.7 g, 22.4 mmol, 81%) (Found: C, 37.9. $C_8H_6F_8$ requires C, 37.8%), b.p. 140° at 755 mmHg, λ_{max} 5.89 μm (C:C str.) (lit.,¹³ for 1H,4H,5H,5H-tetrafluorocyclopentene, (0.8 GeV) (ne., 10 m, m, m, or), or) or consistency of point of (2, 5), 8 μ m), m/e 254 (C₈H₆F₈⁺, 50%), 135 (C₃H₄F₅⁺, 74%), 121 (C₅H₄F₈⁺, 100%), 115 (C₃H₈F₄⁺, 70%), 101 (C₂HF₄, 43%), 95 (C₃H₂F₃⁺, 32%), 85 (C₂H₄F₃⁺, 34%), and 51 (CHF₂⁺, 30%).

Lithium Aluminium Hydride Reduction of Compounds (IV) and (V).-A mixture of (IV) (14.3 g, 35.7 mmol), cis-(V) (51.0 g, 127.5 mmol), and trans-(V) (27.3 g, 68.2 mmol) was added to a well stirred mixture of anhydrous tetrahydrofuran (160 ml) and lithium aluminium hydride (8.5 g, 224 mmol) under reflux. Stirring was continued for 5 h, then tetrahydrofuran (150 ml) was added and the mixture was centrifuged. The clear solution was separated from the aluminium salts, which were extracted twice with tetrahydrofuran. The combined solutions were cautiously diluted with 10% hydrochloric acid and the mixture was allowed to reach room temperature. The organic layer and the ether extracts of the aqueous layer were dried (MgSO₄) and then distilled to give cis-(VI) (33·1 g, 120.7 mmol, 95%), trans-(VI) (13.0 g, 47.4 mmol, 69%), and (X) (6.5 g, 25.6 mmol, 72%).

¹³ W. J. Feast, D. R. A. Perry, and R. Stephens, *Tetrahedron*, 1966, **22**, 433.

Hydrogenation of Compound (VII).—Compound (VII) (37.5 g, 138 mmol) in dry ether (50 ml) was placed in a stainless steel autoclave (200 ml) with Raney nickel (4 g) and enough hydrogen to produce a pressure of 80 kg cm⁻². The autoclave was rocked and heated at 70° for 2 h. Distillation of the products gave a mixture (35 g, 128 mmol, 93%) of cis- and trans-isomers of (VI).

Dehydroiodination of Compound (II).—Compound (II) (9.8 g, 24.5 mmol) was added (1 h), under nitrogen, to a stirred solution of potassium hydroxide (2 g, 35.6 mmol) in ethylene glycol (13 ml) at 130° and the products were continuously distilled off. After being washed with water and dried (MgSO₄) the product (6.2 g) was fractionated to give material (4.3 g, 15.8 mmol, 64%) boiling at 100— 101° and 755 mmHg and unchanged (II) (as residue) (1.8 g, 4.5 mmol.). G.l.c. of the product showed two components (ratio of peak areas 9:1). The separated components (by g.l.c.) were identified as *trans*- and *cis*-isomers of 3,3,4,4,7,7,8,8,8-*nonafluoro-octa*-1,5-*diene* (XII), from i.r., mass, and n.m.r. spectra; m/e 272 (C₈H₅F₉⁺, 0.5%), 77 (C₈H₃F₂⁺, 100%), and 51 (CHF₂⁺, 16%).

3,3,4,4,7,7,8,8,8-Nonafluoro-octane (XIII).— Hydrogenation of compound (XII) (6.0 g, 22.0 mmol) over 5% palladium-carbon (0.5 g) in dry ether (25 ml) at room temperature in a hydrogenation burette was complete in 3 h. Fractionation gave 3,3,4,4,7,7,8,8,8-nonafluorooctane (XIII) [3.8 g, 13.8 mmol, 63% (89% including estimates on forerun and tail fraction)] (Found: C, 34.6; H, 3.4. $C_8H_9F_9$ requires C, 34.8; H, 3.3%), b.p. 40° at 1 mmHg, m/e 276 ($C_8H_9F_9^+$, 0.5%), 79 ($C_3H_5F_2^+$, 100%), and 51 (CF_2H^+ , 13%). Hydrogenation of compound (XI) was effected in the same manner; the i.r. spectrum of the product was identical with that of compound (XIII) and showed it to be olefin-free.

Hydrogenation of Compound (III).—Compound (III) (24 g, 61 mmol) in anhydrous ethanol (50 ml) was placed in a stainless steel autoclave (200 ml) with Raney nickel (4 g) and hydrogen (30 kg cm⁻²). The autoclave was rocked (2 h) and heated at 65° to give 1,1,1,2,2,5,5,6,6,9,9,10,10,10tetradecafluorodecane (XIV) (15.6 g, 39.6 mmol, 65%) (Found: C, 30.6; H, 1.9. $C_{10}H_8F_{14}$ requires C, 30.45; H, 2.05%), m.p. 73—74° (from ethanol), m/e 394 ($C_{10}H_8F_{14}^+$, 0.5%), 197 ($C_5H_4F_7^+$, 100%), 177 ($C_5H_3F_6^+$, 76%), 127 ($C_4H_3F_5^+$, 28%), 77 ($C_3H_3F_2^+$, 25%), and 51 (CHF₂⁺, 20%).

Isomerisation of the Unsaturated Monoadduct (II) to the Cyclic Compound (V) in Cyclohexane Solution.—A mixture of adduct (II) (1.6775 g, 4.193 mmol), cyclohexane (2.4361 g, 28.946 mmol), and di-t-butyl peroxide (0.0311 g, 0.213 mmol), weighed accurately, was placed in tubes that were evacuated, filled with nitrogen twice, and sealed *in vacuo* at -140° . After 2.7, 4.3, and 6.0 h at 120° in an oilbath, the tubes were cooled rapidly and the composition of the products was determined by g.l.c. Peaks corresponding to cyclohexane and *cis*- and *trans*-isomers of (V) were measured. Results were (h; area of *cis*-(V)/area of cyclohexane; area of *trans*-(V)/area of cyclohexane): 0, 0, 0; 2.7, 0.0156, 0.0048; 4.3, 0.0321, 0.0096; 6, 0.0427, 0.0094.

N.m.r. Spectra.—Difficulties arose in assigning the observed resonances to the *cis*- or *trans*-cyclobutane isomers (V) and (VI), and distinguishing between the two diffuoromethylene groups in the same ring system. Ambiguities could not be completely resolved and alternative method

		TABLE	3		Ū	·	,	
Compound	Nuclei	Intensity τ		 \$	Splitting	$J/{ m Hz}$		
c lm cd b fg hi a (II)	a b	1	5·39 5·39		dddd	$\begin{array}{l} \mathbf{H_bF_g}\\ \mathbf{H_bF_f} \end{array}$	$21 \cdot 7$ $6 \cdot 7$ $7 \cdot 0$	
	c, d	2	6.4 - 7.5	00 75	Complex m		2.0	
	e f	3 1		86.75 95.4	s dt	$F_{f}F_{g}$	270	
	g	1		116.0	ddd	F _g F _f F _g H _b	270 22·0	
	h	1		109.8	d of br t	F_hF_i	263 5.0	
	i	1		110.9	dt	F_iF_h	263 8·0	
	1	1		117.2	ddd quin.	F_lF_m	$266 \\ 23.0 \\ 9.8$	
	m	1		120.2	ddd	F_mF_l	$1.7 \\ 266 \\ 24.0 \\ 11.0$	
$CF_3 \cdot CF_2 \cdot CH_2 \cdot CH_2 \cdot CF_2 \cdot CF_2 \cdot CH \cdot CH \cdot CF_2 \cdot CF_3$ e i b c h f a g d (III)	a b, c d	2 4 3	3·3—3·9 7·64	85.7	Complex m Complex t Complex t	$\mathbf{H_bF_i} = \mathbf{H_cF_h}$	ca. 15 1·8	
()	f, h g i	3 4 2 2		80.4 115.4 118.0 119.5	Complex m Complex m Complex t	F_iH_b	15.5	
	a b, c, d, d' e	1 5 3	5·7 6·6—8·2	86·55	Complex m Complex m S			
e Im cH I fF Fh	h i	1		109.5 126.3	d of complex m d of complex t	$\mathbf{F_hF_i}$ $\mathbf{F_iF_h}$	239 239	
gF [*] Fi (IV)	f	1		112.3	ddd	$F_{i}F_{g}$	$ \begin{array}{r} 11.0 \\ 232 \\ 18.0 \\ 9 \end{array} $	
	g	1		118-3	d of br t	$F_{g}F_{f}$	233 10·0	
	1	1		115.7	ddd	F_1F_m	266 27·7	
	m	I		119-9	dddd	F_mF_1	266 $25 \cdot 4$ $10 \cdot 5$ $2 \cdot 5$	
d d′ CF3·CFF·CHH CH2I	a b, c, d, d'	2 4	6·75 7·1—7·7		d Complex m	H_aH_b	$7 \cdot 2$	
e lm cH Hb	e h	$\frac{3}{1}$		86·3 109·8	s dq	F_hF_i	213	
gF Fi	i f	1 1		135·3 111·0	d of complex m d of br q	$\mathbf{F_i F_h}$ $\mathbf{F_t F_g}$	213 212	
(Y) <i>cis</i> -isomer	g l m	1 1 1		132.7 117.6 118.1	d of complex m Complex m Complex m	$F_{g}F_{f}$	9 212	
	a b, c d, d'	2 2 2 3	6·75 6·85 7·55	86.3	d Complex m Complex m	H_aH_b	7.0	
	f g	1 1		113.3 125.8	d of complex m dq	$\mathbf{F_fF_g}$ $\mathbf{F_gF_f}$	216 215	
(Y) trans-isomer	h i	1 1		$113.3 \\ 127.7$	d of complex m dq	$\mathbf{F_hF_i}$ $\mathbf{F_iF_h}$	216 216	
	1	1		117.8	dtd	F_iF_m	8 260 16·8	
	m	1		118-4	dtd	F_mF_1	1.6 260 16.8 1.6	

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¹ 8.							000
	TABL	. Е. З. (С.	ontinued)		0.1111	7.17	т
Compound	Nuclei	Intensity	τ	ϕ^*	Splitting	J/1	lz
	b, c, d, d'	4	6·88·0 8·78		Complex m	н н,	6.5
	e	3	010	86.5	s	11a11D	00
cH Hb	f	1		111.6	d of overlapping dt	F_hF_i	210
fF Fh							12
gF Fi	g	1		135.3	d of complex m	F_iF_h	210
(VI) signisomor	ĥ	1		111.0	d of overlapping dt	$F_{f}F_{g}$	212
(11) 0/3-1301161							10
	l, m	2	C	ca. 119	Complex m		0
d d '	b, c	2	7.00		Complex m		
CF3 CFF CHH H	d, d'	2	7.75		br t d	н н.	19
^{с ст} сн Снз	e	3	0.00	86.5	s	11a11b	•
fF C	f	1		109.6	d of quin.	$F_{f}F_{g}$	211
	α	1		127.8	d of complex m	F.F.	$\frac{10}{211}$
g	ĥ	i		118.1	d of complex m	$F_{h}F_{i}$	211
(VI) <i>trans</i> -isomer	i	1		125.0	d of br t	F_iF_h	211
	1 m	2		118.0	d of t of complex m	F ₁ F _m	ca. 260
	1, 111	4		110 0	d of t of complex m	- 1- m	18.5
H_	a	1	4 ·09		Complex m		
dd' ja	b	1	4.38		quin.		$2 \cdot 2$
CF3 · CFF CHH	C A AV	1	6.43		Complex m		
e (m _c H	u, u e	$\frac{2}{3}$	1.02	86.43	s		
rF Fh	f	1		113.8	d of br d	$F_{f}F_{g}$	211
^E Fi	a	1		120.6	d of complex m	FF.	12·5 211
· · · · ·	s h†	1		114.5	d of br m	$F_h F_i$	226
	i †	1		116.3	d of br m	F_iF_h	226
	1	I		117.0	dtd	F_1F_m	266
							3.6
	m	1		118.1	dtd	F_mF_l	266
							16 5
	1	,	9.04		J	TTE	94
CF3 Hb CU	D a	3	3·94 8·0		Complex m	п _b г _е	94
	с	3		$73 \cdot 43$	d	$F_{e}F_{e}$	9.8
er l	d	2		113.95	Complex m	Fo H.	32.6
F F	е	1		110.32	urqq	Fe _e F _d	12.8
Fa tF						F _e F _c	9.8
(1177)	r	a		117.41	he to	Fe _e H _a	1.8
	1	2		117.41	bitu	L ⁴ L ⁴	4·0
	ь	1	4.00		đ	нг	36.5
CF3 Hb	d, d'	4	4.00 5.96		Complex m	IIbr e	30.9
	a	3	8.08		Complex m		10.0
C	C t	3		73.1	d of br m	F _e F _e	10.8
F	e	ĩ		119.01	d of q	F.H.	36.5
Ft Ft					*	F_eF_c	10.8
d' (IX)							
-		_			_		
	a bodd	1	4.46		br s Complex m		
CF3 CFF CHH	ь, с, ц, ц е	3	0.90.2	86.63	s		
° ^ເ ™ ҫႾַๅ๎ ׀	f	1		102.61	d of complex m	$\mathbf{F}_{\mathbf{f}}\mathbf{F}_{\mathbf{g}}$	252
۲ <u>۲</u> ۲۰۰۰۲	S F	1		107.01	d of complex m	$F_{g}F_{f}$ F.F	252 268
gר ⊏h ייסדי	11	T		110.19	uuu	+ 1+ m	25.0
(A)				110.00		T T	10.0
	m	1		118.86	ddd quin.	$\mathbf{F}_{\mathbf{m}}\mathbf{F}_{\mathbf{l}}$	268 25.0
							13.0
	1 +			142 1	1.1.3.1		2
	n ‡	I		142-1	aaad		$17.3 \\ 13.0$

 $13.0 \\ 7.5 \\ 5.3$

	T_A	ABLE 3 (C	continued)				
Compound $CF_3 \cdot CF_2 \cdot CH_2 \cdot CH_2 \cdot CF_2 \cdot CF_2 \cdot CH_2$ d h b c f e a (XI)	Nuclei a b, c d e f h	Intensity 3 4 3 2 2 2 2	${5 \over 3.9 - 4.5} {7.67}$	ϕ^* 86.25 115.53 116.27 119.57	Splitting Complex m Complex m s br m br m br t	$F_{h}H_{b}$	J/Hz caj. 15
$\begin{array}{c} CF_3 \cdot CF_2 \cdot CH \cdot CH \cdot CF_2 \cdot CF_2 \cdot CH \cdot CH_2 \\ c & f & d & e \\ & & & & \\ & & & \\ & & & \\ & & & \\ &$	a b c d e f	2 3 2 2 2	3·29—3·89 3·9—4·4	$\begin{array}{c} 85 \cdot 75 \\ 115 \cdot 0 \\ 115 \cdot 7 \\ 118 \cdot 0 \end{array}$	Complex m Complex m Complex t Complex m d of overlapping t d of overlapping oct.	F _c F _t	1.8 9 3.5 8.0 1.8
$\begin{array}{ccc} CF_3 \cdot CF_2 \cdot CH: CH \cdot CF_2 \cdot CF_2 \cdot CH: CH_2 \\ c & f & d & e \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & &$	a, b c d f e	$6\\3\\2\\2\\2$	3.5-4.4	$\begin{array}{r} 85{\cdot}8\\ 110{\cdot}13\\ 112{\cdot}43\\ 114{\cdot}86\end{array}$	Complex m br m Complex m Complex m Complex m		
$\begin{array}{ccc} CF_3 \cdot CF_2 \cdot CH_2 \cdot CH_2 \cdot CF_2 \cdot CF_2 \cdot CH_2 \cdot CH_3 \\ e & b & f & g & c & d \\ & & & & & & & & \\ & & & & & & & &$	a, b, c d f g h	6 3 3 2 2 2 2	$\begin{array}{c} 7{\cdot}4{-\!-\!8{\cdot}2}\\ 8{\cdot}92 \end{array}$	$86.5 \\ 116.2 \\ 117.5 \\ 119.5$	Complex m t s br m Complex m Complex t	$F_{h}H_{a}$	7.5 cal. 15
$\begin{array}{c} CF_3 \cdot CF_2 \cdot CH_2 \cdot CH_2 \cdot CF_2 \cdot CF_2 \cdot CH_2 \cdot CH_2 \cdot CF_2 \cdot CF_3 \\ c & e & b & d & d & b & a & e & c \\ \end{array} $ (XIV)	a, b c d e	$3 \\ 2$	7.67	86·33 116·03 119·38	Complex m s br m Complex t	FeHa	ca. 17

† For 1-methylene-2,2,3,3-tetrafluorocyclobutane ϕ^* 117.2 (D. R. Taylor and M. R. Warburton, *Tetrahedron Letters*, 1967, 3277). ‡ For 1*H*,4*H*,5*H*-tetrafluorocyclopentene ϕ^* 141.6 (ref. 12).

of assignment had to be considered. We have followed the criteria derived from fluorine chemical shift calculations,¹⁴ which show that relative fluorine chemical shifts are mainly determined by the electric field effect of neighbouring groups. According to these calculations, a fluorine paramagnetic shift is expected to be more pronounced, the more polarisable and nearer to the resonant fluorine nuclei the neighbouring group is. Since the substituents of our cyclobutanes are likely to be in the following order of polarisability: $CH_2I > CH_2 \cdot CF_2 \cdot CF_3 >$ CH₃, the relative chemical shift of geminal fluorines in CF_2 groups adjacent to such substituents is expected, for example, to be greater for CF_2 ·C·CH₂I than for CF_2 ·C·CH₃. The assignments reported in Table 3 have been made accordingly. The cis- or trans-disubstituted structures of (V) and (VI) have been assigned on the same basis, namely

that the internal chemical shift for the two geminal fluorines of the ring CF_2 groups is expected to be greater for the *cis*configuration. In other words in the *cis*-isomer the effect of the two substituents is additive on the same geminal fluorine nucleus, whereas in the *trans*-isomer the becomes partially compensated. For (VII), the CF_2 group near the asymmetric carbon centre will give the largest internal chemical shift.

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¹⁴ J. Feeney, L. H. Sutcliffe, and S. M. Walker, *Mol. Phys.*, 1966, **11**, 117.