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Polyfluorocyclopentadienes. Part II.¹ The Thermal Dimer of Perfluorocyclopentadiene: Perfluoro(tricyclo[5,2,1,0^{2,6}]deca-3,8-diene)

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Perfluorocyclopentadiene dimerises readily to perfluoro(tricyclo[5,2,1,0^{2,6}]deca-3,8-diene), the structure of which was proved by chemical methods and by infrared, nuclear magnetic resonance, and mass spectroscopy. Pyrolysis of the dimer effects its breakdown by a retro-Diels-Alder cleavage to perfluorocyclopentadiene, accompanied by elimination of difluorocarbene and formation of tetrafluoroethylene and perfluoro(bicyclo[4,3,0]nona-2,4,7-triene). Pyrolysis of the last product over mild steel gives perfluoroindane and a compound believed to be perfluoroindene.

Dehalogenation with zinc dust of a trichloroheptafluorocyclopentane from the reaction of perchlorocyclopentadiene with cobalt trifluoride gives perfluorocyclopentadiene and 4-chloroheptafluorocyclopentene, oxidation of which affords β-chloropentafluoroglutaric acid. Direct fluorination of perchlorocyclopentadiene in 1,1,2trichlorotrifluoroethane gives low yields of tetrachlorohexafluorocyclopentane and trichloroheptafluorocyclopentane.

PERFLUOROCYCLOPENTADIENE^{1,2} is best prepared¹ by of tetrachlorohexafluorocyclozinc-dechlorination pentane obtained by fluorination of perchlorocyclopentadiene with cobalt trifluoride; the overall yield of the fluoro-diene is 15%, but this is increased to ca. 25% when the halogenocyclopentanes $C_5F_xCl_y$ (x < 6; x + y = 10) formed with the tetrachlorocompound C₅F₆Cl₄ are diluted with perchlorocyclopentadiene and recycled through the cobalt fluoride reactor.

In an attempt to increase further the efficiency of this method, a study was made of the dehalogenation to perfluorocyclopentadiene of a trichloroheptafluorocyclopentane fraction produced in ca. 5% yield in the perchlorocyclopentadiene-cobalt trifluoride reaction.¹ Zinc dust in dioxan gave perfluorocyclopentadiene, but in only 9% yield, and the main product (50% yield) was 4-chloroheptafluorocyclopentene, permanganateoxidation of which afforded β-chloropentafluoroglutaric acid; thus it seems that the trichloroheptafluorocyclopentane must have been essentially the 1,2,4-trichloroisomer (see equation 1).



Direct liquid-phase fluorination of perchlorocyclopentadiene dissolved in 1,1,2-trichlorotrifluoroethane was investigated briefly in an attempt to provide an alternative route to the tetrachlorohexafluorocyclopentane precursor of perfluorocyclopentadiene; only a trace of this compound was formed, together with trichloroheptafluorocyclopentane (3%) yield) and much high-boiling material.

Perfluorocyclopentadiene is a colourless volatile liquid,

b. p. 28°, the vapour of which absorbs strongly in the infrared region at 5.65μ (•CF=CF• stretching). Its mass spectrum contains prominent peaks corresponding to the ions $C_5F_6^+$, $C_5F_5^+$, $C_4F_4^+$ (base peak), $C_3F_3^+$, and CF_3^+ , while its ¹⁹F n.m.r. spectrum consists of three absorption regions of equal relative intensities centred at 61.2, 78.2, and 94.4 p.p.m., respectively, to high field of external trifluoroacetic acid, which are assigned, in order, to the difluoromethylene fluorines, the vinylic fluorines of type :CF·CF₂, and the vinylic fluorines of the :CF•CF: group.³

Photochemical chlorination of perfluorocyclopentadiene with an excess of chlorine gives 1,2,3,4-tetrachlorohexafluorocyclopentane in 92% yield,1 but use of an equimolar ratio of reactants yields as major product (86%) a mixture of cis-3,5-, trans-3,5-, cis-3,4-, and trans-3,4-dichlorohexafluorocyclopentene which could not be separated by gas-liquid chromatography (g.l.c.).

Perfluorocyclopentadiene dimerises when stored either in the vapour phase in the absence of air or as a liquid under nitrogen,¹ thus resembling cyclopentadiene⁴ but not perchlorocyclopentadiene.⁵ Four samples of perfluorocyclopentadiene underwent 9, 62, 82, and 94%transformation into dimer after being stored, respectively, at temperatures of -22, 19, 70, and 138° for 24 hr.; dimerisation of the diene can be prevented by storing it at -196° . The dimer is a colourless waxy solid, m. p. $42.5-43.0^{\circ}$, which is characterised by a strong ·CF=CF· stretching band at 5.72 μ in the i.r. region and gives only one peak when examined by g.l.c. techniques. Titration of the dimer against potassium permanganate in acetone showed it to be a diene, and this is confirmed by the formation of a saturated tetrachloride when the dimer is chlorinated photochemically.

In view of the dienic nature of perfluorocyclopentadiene dimer, and considering the modes of thermal dimerisation of polyfluoro-olefins,⁶ perfluorobutadiene,⁷ and cyclopentadiene or its derivatives,⁴ four structures (I—IV) were considered for the dimer of perfluorocyclo-

¹ R. E. Banks, R. N. Haszeldine, and J. B. Walton, J. Chem. Soc., 1963, 5581.

 ² J. Burdon, T. M. Hodgins, D. R. A. Perry, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 1965, 808.
 ³ K. G. Orrell, unpublished results.

 ⁴ R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of kenes," ed. S. Patai, Interscience, London, 1964, p. 878.
 ⁵ H. E. Ungnade and E. T. McBee, *Chem. Rev.*, 1958, 58, 249.
 ⁶ J. D. Roberts and C. M. Sharts, *Org. Reactions*, 1962, 12, 1.
 ⁷ I. L. Karle *et al.*, *J. Amer. Chem. Soc.*, 1964, 86, 2523. Alkenes.

pentadiene. On the basis of ¹⁹F n.m.r. and mass spectrometric measurements, coupled with the results of pyrolysis experiments, structure (I), perfluoro(tricyclo- $[5,2,1,0^{2,6}]$ deca-3,8-diene), is assigned; thus perfluorocyclopentadiene is the first perfluoro-1,3-diene to undergo a Diels-Alder type of dimerisation.



The ¹⁹F n.m.r. spectrum of perfluorocyclopentadiene dimer, measured relative to external trifluoroacetic acid, was analysed only after study of the spectra of other Diels-Alder adducts derived from perfluorocyclopentadiene.8,9 The four lowest field bands comprise an AB pattern centred at 32·2 p.p.m. [$|J_{gem}| = 260$ c./sec.; $(v_0\delta) = 12.9$ p.p.m.] caused by the two non-equivalent fluorines of the difluoromethylene group of the dienophilic residue (V), while the next four bands form an AB pattern centred at 52·4 p.p.m. [$|J_{gem}| = 180$ c./sec.; $(v_0\delta) = 13.2$ p.p.m.] and are due to the fluorines of the diffuoromethylene group of the diene residue (VI). Eight bands, each of unit intensity, occur at 63.0, 65.8, 66.6, 73.2, 105.2, 114.8, 140.2, and 142.8 p.p.m.; the last two are assigned to the tertiary fluorines of the type present in (VI), while the 105.2 and 114.8 p.p.m. bands are attributed to the tertiary fluorines of the type present in (V), and the remaining four bands are associated with the four vinylic fluorines of structure (I). Detailed analysis of the fine structure of the spectrum ¹⁰ shows that the dimer probably has the endo configuration.



The mass spectrum of perfluorocyclopentadiene dimer is fully consistent with structure (I) although it cannot exclude the possibility of structure (II); the base peak corresponds to the ion $C_5F_6^+$, presumably from a retro-Diels-Alder cleavage, while the molecular ion is very abundant and a prominent peak at m/e 298 is readily correlated with loss of a diffuoromethylene fragment from the molecular ion (see equation 2).

Perfluorocyclopentadiene dimer shows high thermal stability: it is unaffected by storage at 475° for 45 min. in a platinum thimble encased in silica. However, under flow conditions in silica at $555^{\circ}/2$ —3 mm. with a

contact time of ca. 2 sec., 5% breakdown of the dimer occurs with formation of perfluorocyclopentadiene and traces of tetrafluoroethylene. At higher temperatures more complete breakdown occurs, and the products are

$$\begin{bmatrix} F & F & F \\ F & F_2 & F \\ F & F_2 \end{bmatrix}^+ \xrightarrow{-CF_2} \begin{bmatrix} F & F \\ F & F_2 \\ F & F_2 \end{bmatrix}^+$$
(2)

tetrafluoroethylene, perfluorocyclopentadiene, perfluoro-(bicyclo[4,3,0]nona-2,4,7-triene) (VII), and unidentified compounds; for example, pyrolysis of the dimer in platinum at $680^{\circ}/2$ mm. with a contact time of 0.3 sec. gives unchanged starting material (24% recovery) together with (yields based upon dimer consumed and the stoicheiometry of equation 3) tetrafluoroethylene (38%), perfluorocyclopentadiene (22%), perfluoro(bicyclo[4,3,0]nona-2,4,7-triene) (40%), and unidentified material which may arise through reactions between the dimer, perfluorocyclopentadiene, or the triene (VII) and diffuorocarbene, presumed to be formed in the pyrolysis. These results are fully consistent with structure (I) for the thermal dimer of perfluorocyclopentadiene. The high thermal stability of (I) is in marked contrast to that of dicyclopentadiene, which readily regenerates cyclopentadiene when heated to 160°.



Perfluoro(bicyclo[4,3,0]nona-2,4,7-triene) (VII) is a liquid, b. p. $129^{\circ}/774$ mm., which shows three $\cdot CF=CF \cdot$ stretching bands in the i.r. region [5.65, 5.70 μ (doublet), and 5.86 μ ; cf. perfluorocyclohexa-1.3-diene,¹¹ 5.70, 5.84 $\mu,$ and perfluorocyclopentene, 5.65 $\mu]$ and gives a hexachloride ${\rm C_9Cl_6F_{10}}$ quantitatively when chlorinated photochemically. Its ultraviolet, ¹⁹F n.m.r., and mass spectra are fully consistent with structure (VII): its u.v. spectrum (solution in ethanol) contains a maximum at 262 mµ (ε 2280) [cf.¹¹ perfluorocyclohexa-1,3-diene, $\lambda_{\text{max.}}$ (ether) 256 mµ (ε ca. 3160)], while its ¹⁹F n.m.r. spectrum, measured relative to external trifluoroacetic acid, shows an AB pattern centred at 29.5 p.p.m. $|J_{\text{gem}}| = 270 \text{ c./sec.}; \text{ total integrated intensity} = 2.00$ as expected 9 for a compound containing a difluoromethylene group situated in a residue of type (V), and eight absorption systems each of unit intensity at 65.0, 76.9, 77.6, 78.8, 79.3, 81.3, 88.2, and 105.8 p.p.m.; the base peak in the mass spectrum of (VII) corresponds to

⁸ R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G. Orrell, *Chem. Comm.*, 1965, 41.
⁹ R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G.

⁹ R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G. Orrell, to be published.

¹⁰ R. Fields, M. Green, and A. Jones, in the press.

¹¹ D. E. M. Evans and J. C. Tatlow, J. Chem. Soc., 1954, 3779.

the CF⁺ ion, while, as expected for a highly unsaturated cyclic fluorocarbon,¹² the molecular ion $(C_9F_{10}^+)$ is intense and principal peaks also occur at m/e values corresponding to the ions $C_9F_9^+$, $C_8F_8^+$, $C_8F_7^+$, and $C_3F_4^+$.

A single attempt was made to defluorinate triene (VII) to perfluoroindene (VIII) by passing it over mild steel at 490-495°; separation of the product by gas-liquid chromatography afforded the known perfluoroindane¹³ (IX), isomeric with (VII), in 28% yield based on 80% conversion of the triene (VII), and traces of a pale vellow liquid which had a carbon content close to that expected for perfluoroindene and an i.r. spectrum showing •CF=CF• absorption at 5.77 μ and aromatic bands at 6.63, 6.68, and 6.91 μ . That this last product was probably perfluoroindene is supported by its mass spectrum, which showed prominent peaks at m/e values corresponding to the ions $\mathrm{C_9F_7^+},~\mathrm{C_8F_6^+},~\mathrm{C_7F_4^+},$ and $C_7F_{3}^{+}$ and in which the base peak corresponded to the molecular ion $C_9F_8^+$; not enough material was available for n.m.r. measurements. Rearrangements of C₆ alicyclic fluorocarbons or their derivatives on treatment with hot metals are known,¹⁴ and fluoride-ion initiated isomerisation via perfluorocarbanions appears likely (see Scheme). Others ² have recently reported that the



fluorination of perfluorocyclopentadiene dimer with cobalt trifluoride gives a saturated fluorocarbon $C_{10}F_{16}$ identical with a product obtained in low yield by similar fluorination of *endo*-tricyclo[5,2,1,0^{2,6}]decane; this agrees with the assignment of (I) for the structure of the dimer.

EXPERIMENTAL

Perfluorocyclopentadiene is volatile (b. p. 28°) and susceptible to attack by moist air, so it was manipulated in a Pyrex vacuum system and stored therein at -196° to prevent dimerisation. The identities of products were established by molecular weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), u.v. spectroscopy (Unicam S.P. 700 spectrophotometer),¹⁹F n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 56.46 Mc./sec.), mass spectrometry (A.E.I. MS/2H spectrometer) and gas-liquid chromatography (Perkin-Elmer Fraktometer model 116).

Perfluorocyclopentadiene and trichloroheptafluorocyclopentane were prepared as described previously.¹ Mass spectral data for the diene are listed in Table 1.

TABLE 1

mass spectral data for permastory dopentation	Mass	spectral	data for	perfluorocy	vclo	pentadien
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	Assign-	Abund-		Assign-	Abund-
m e	ment	ance	m e	ment	ance
31	CF^+	$24 \cdot 4$	105	$C_{4}F_{3}^{+}$	15.1
55	$C_{a}F^{+}$	6.1	117	$C_5F_3^+$	3.0
69	CF_{3}^{+}	29.4	124	$C_{\mathbf{A}}F_{\mathbf{A}}^{+}$	$100 \cdot 0$
74	$C_3 \tilde{F}_2^+$	7.6	143	$C_{4}F_{5}^{+}$	$3 \cdot 3$
86	$C_{4}F_{2}^{+}$	$3 \cdot 9$	155	$C_{5}F_{5}^{+}$	$42 \cdot 4$
93	$C_{3}F_{3}^{+}$	$33 \cdot 6$	174	$C_{5}F_{6}^{+}$	73.7

Dechlorination of Trichloroheptafluorocyclopentane (with J. B. Walton).---Using the techniques employed for the conversion of tetrachlorohexafluorocyclopentane into perfluorocyclopentadiene,¹ trichloroheptafluorocyclopentane (30.0 g.) in dioxan (8 ml.) was added dropwise during 30 min. to a stirred suspension of activated zinc dust (30 g.) in refluxing dioxan (20 ml.). Distillation of the product which collected at -72° or -196° , using a 15×1 cm. adiabatic column packed with Heli-pak Hastelloy B wire coils $(0.05 \times 0.10 \times 0.10$ in.), gave perfluorocyclopentadiene (1.5 g.; 9%), b. p. 28°, and 4-chloroheptafluorocyclopentene (11.3 g.; 50%) pure by g.l.c., but slightly impure analytically (Found: C, 28.8%; M, 228. Calc. for C₅ClF₇: C, 26·3%; M, 229), b. p. 54—56°, λ_{max} , 5·65 μ (·CF=CF· str.; vapour). The ¹⁹F n.m.r. spectrum of 4-chloroheptafluorocyclopentene, measured using trifluoroacetic acid as external reference, consisted of an AB pattern centred at 35.5 p.p.m. due to the non-equivalent fluorines of the two CF₂ groups, a 53.8 p.p.m. band assigned to the fluorine nucleus of the CFCl group, and a band at 75.8 p.p.m. attributed to the equivalent vinylic fluorines, since the vinylic fluorines in perfluorocyclopentene give rise to a band at 75.8 p.p.m.; ³ the relative intensities of the three absorption regions was 4.00: 1.02: 1.97, and several weak impurity bands were present in the spectrum.

Oxidation of 4-Chloroheptafluorocyclopentene.—4-Chloroheptafluorocyclopentene (0.972 g.) was dissolved in a solution of potassium permanganate (1.425 g.) in acetone (200 ml.). After 30 min., the brown product was treated with water (200 ml.) then heated *in vacuo* to remove acetone. The remaining aqueous suspension was acidified (H₂SO₄), decolorised with sulphur dioxide, and finally extracted with ether (4×50 ml.); the ethereal extract was dried (MgSO₄) and treated with aniline (2 g.), to give dianilinium β -chloropentafluoroglutarate (1.030 g.; 55%) (Found: C, 46·1; H, 3·8; N, 6·4%; Equiv., 218. C₁₇H₁₆ClF₅N₂O₄ requires C, 46·1; H, 3·6; N, 6·3%; Equiv., 221), m. p. 219—221° after recrystallisation thrice from 1: 1 acetone–chloroform. Treatment of an aqueous solution of the dianilinium salt with aqueous S-benzylthiouronium chloride gave the corre-

¹³ D. Harrison, M. Stacey, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 1963, **19**, 1893.

¹⁴ R. E. Banks *et al.*, Nature, 1958, **183**, 586; C. R. Patrick *et al.*, Chem. and Ind., 1963, 1557.

¹² J. R. Majer, in "Advances in Fluorine Chemistry," ed. M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths, London, 1961, vol. 2, p. 55.

sponding di-(S-benzylthiouronium) salt (Found: C, 42.9; H, 4.0; N, 9.6. $C_{21}H_{22}ClF_5N_4O_4S_2$ requires C, 42.8; H, 3.7; N, 9.5%), m. p. 195.0—196.5° after recrystallisation thrice from water.

Direct Fluorination of Perchlorocyclopentadiene.—Fluorine (31 g., 0·82 mole) diluted with nitrogen in the molar ratio of 1:4 ($F_2: N_2$) was bubbled during 8 hr. through a stirred solution of perchlorocyclopentadiene (25·0 g., 0·092 mole) in 1,1,2-trichlorotrifluoroethane (25 ml.). Distillation of the product afforded: (i) a mixture (1·6 g.), b. p. 82— 98°/30 mm., which was shown by g.l.c. and i.r. analysis to contain 1,2,3,4-tetrachlorohexafluorocyclopentane (ca. 0·1 g.; 1% yield), 1,2,4-trichloroheptafluorocyclopentane (ca. 0·8 g.; 3%), and several unknown higher-boiling compounds; (ii) a fraction (5·4 g.) which, from its boiling range (98—126°/30 mm.) and i.r. spectrum, probably consisted of hexachlorodifluorocyclopentenes; (iii) unknown material (10·1 g.), b. p. 126—136°/30 mm.; and (iv) a yellow gluelike stillpot residue (8 g.).

Reactions of Perfluorocyclopentadiene.—(a) Chlorination. A mixture of chlorine (1.05 g., 14.8 mmoles) and perfluorocyclopentadiene (2.57 g., 14.8 mmoles), contained in a 100-ml. Pyrex ampoule, was irradiated during 20 hr. with light from a 100-w tungsten-filament lamp placed 30 cm. distant. G.l.c. analysis [2 m. di-(2-ethylhexyl)sebacate-Celite, 40° of the volatile product revealed the presence of only two components: perfluorocyclopentadiene (0.18 g., 1.03 mmoles; 7% recovery) and a material (3.10 g., 12.65 mmoles; 86% yield) which was isolated by distillation and shown by analysis (Found: C, 24.3%; M, 243. $C_5Cl_2F_6$ requires C, 24.5%; M, 245), i.r. spectroscopy (•CF=CF• str. at 5.68μ), and ¹⁹F n.m.r. spectroscopy to be a mixture, b. p. $87.4^{\circ}/760$ mm., $n_{D}^{19.5}$ 1.3697, of cis-3,5-, trans-3,5-, cis-3,4-, and trans-3,4-dichlorohexafluorocyclopentene [(X), (XI), (XII), and (XIII), respectively]. (A 3,4-dichlorohexafluorocyclopentene, b. p. 87.5–88°, λ_{max} $5.65 \,\mu$, of unstated geometry has been reported previously.²)



The ¹⁹F n.m.r. spectrum of the dichlorohexafluorocyclopentene mixture, measured relative to external $CF_3 \cdot CO_2H$, shows three AB patterns of relative intensities 2:1:ca. $\frac{1}{2}$ centred at 34.6, 40.0, and 35.0 p.p.m., respectively, the last of which is relatively difficult to detect. In addition, nine strong absorptions, each of unit intensity, occur at 21.8, 36.4, 38.6, 39.8, 41.8, 68.0, 72.4, 73.4, and 77.6 p.p.m., the last four being in the region expected for vinylic fluorines. Consideration of the chemical shifts and the splittings of each of the absorptions has allowed assignments to be made for the four single fluorines of one of the ABGMPX system, the three pairs of fluorines in the AA'PP'XX' system, and the PP'XX' pairs in the ABPP'XX' system.¹⁵ 6 z The remaining weak bands (each of relative intensity $ca. \frac{1}{4}$) in the spectrum, some of which are obscured, are believed to belong to the second ABGMPX system. The proportions of the isomers may thus be deduced from the integrated areas of the signals to be (X): (XI): (XII) or (XIII): (XIII) or (XIII) = 2:2:4:1, even in the absence of a complete analysis of the spectrum.

1,2,3,4-Tetrachlorohexafluorocyclopentane (0.34 g., 1.07 mmoles; 8%) was recovered from the reaction vessel.

(b) Dimerisation. Four samples of perfluorocyclopentadiene (each 0.339 g., 1.95 mmoles), condensed into 50-ml. Pyrex tubes in vacuo at -196° , were kept at -22, 19, 70, and 138° severally for exactly 24 hr. They were then cooled rapidly to -196° and each product was fractionated in vacuo by the trap-to-trap condensation technique to separate unchanged perfluorocyclopentadiene from its dimer, perfluoro(tricyclo[5,2,1,0^{2,6}]deca-3,8-diene) (Found: C, 34.8%; *M*, 340. Calc. for C₁₀F₁₂: C, 34.5%; *M*, 348), m. p. 42.5-43.0°, b. p. 117-118°/767 mm. (Siwoloboff), λ_{max} , 5.72 μ (-CF=CF· str.). The results are given in the Discussion section.

The mass spectrum of perfluoro(tricyclo[5,2,1,0^{2, 6}]deca-3,8-diene) is described in Table 2.

 TABLE 2

 Mass spectral data for perfluoro(tricyclo[5,2,1,0^{2,6}]

deca-3	,8-di	iene)
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	Assign-	Abund-		Assign-	Abund-
m e	ment	ance	m e	ment	ance
31	CF^+	6.0	172	C _e F ₄ +	0.9
55	$C_{2}F^{+}$	1.0	174	$C_{\mathbf{s}}F_{\mathbf{c}}^{+}$	100.0
69	ĊĔ _a +	$23 \cdot 2$	179	$C_{7}F_{5}^{+}$	11.0
74	C,F,+	2.7	186	$C_{e}F_{e}^{+}$	4.7
79	C ₅ F+	1.3	191	$C_{s}F_{5}^{+}$	1.5
86	C₄F₀+	1.4	193	$C_5F_7^+$	2.5
93	$C_3F_3^+$	13.7	198	$C_7 F_6^+$	3.4
98	$C_5F_2^+$	1.8	203	$C_{9}F_{5}^{+}$	0.5
105	$C_{4}F_{3}^{+}$	3.8	205	$C_{6}F_{7}^{+}$	1.3
110	$C_{6}F_{2}^{+}$	1.1	210	$C_8F_6^+$	12.9
112	$C_3F_4^+$	5.5	217	$C_{7}F_{7}^{+}$	8.1
117	$C_{5}F_{3}^{+}$	8.9	222	$C_{9}F_{6}^{+}$	0.5
122	$C_7F_9^+$	1.0	229	$C_8F_7^+$	20.4
124	$C_4 F_4^+$	28.1	236	$C_7F_8^+$	0.7
129	$C_{6}F_{3}^{+}$	1.9	241	$C_9F_7^+$	7.7
131	$C_{3}F_{5}^{+}$	4.6	248	$C_8F_8^+$	9.8
136	$C_{5}F_{4}^{+}$	1.0	260	$C_9F_8^+$	11.7
141	$C_7F_3^+$	4.8	267	$C_8F_9^+$	1.0
143	$C_{4}F_{5}^{+}$	$2 \cdot 5$	279	$C_9F_9^+$	40.6
148	$C_{6}F_{4}^{+}$	$2 \cdot 1$	298	$C_{9}F_{10}^{+}$	7.1
155	$C_5 F_5^+$	16.9	329	$C_{10}F_{11}^{+}$	11.0
160	$C_{7}F_{4}^{+}$	3.0	348	$C_{10}F_{12}^{+}$	30.6
167	$C_{6}F_{5}^{+}$	1.6			

Reactions of Perfluoro(tricyclo[5,2,1,0^{2,6}]deca-3,8-diene).— (a) Chlorination (with V. Matthews). A solution of perfluorocyclopentadiene dimer (2·1 g., 6·04 mmoles) in perfluoro-n-pentane (5 ml.) and an excess of chlorine (1·48 g., 20·8 mmoles), sealed in a 300-ml. Dreadnought tube, were exposed to daylight for 15 hr. and then shaken with mercury, to give a colourless liquid which was distilled to remove perfluoro-n-pentane, leaving a colourless oil (2·452 g.) (Found: C, 27·6; Cl, 20·1. Calc. for C₁₀F₁₂Cl₂: C, 28·6; Cl, 17·0. C₁₀F₁₂Cl₄ requires C, 24·6; Cl, 29·0%) which was unsaturated in part since its i.r. spectrum contained a ·CF=CF· band at 5·65 μ . A sample of this oil (2·223 g.), dissolved in perfluoro-n-pentane (5 ml.), and chlorine (1·48 g., 20·8 mmoles) were sealed in a 300-ml. Dreadnought tube and irradiated with light from three

¹⁵ R. Fields and A. Jones, private communication.

tungsten-filament lamps (220 w total; 7 cm. distant) for 3 days; the product was shaken with mercury to destroy the excess of chlorine and then evaporated *in vacuo* to remove perfluoro-n-pentane, leaving *perfluoro*(3,4,8,9-*tetrachlorotricyclo*[5,2,1,0^{2,6}]*decane*) (2·401 g., 4·90 mmoles; >81%) (Found: C, 24·3; Cl, 28·9. C₁₀Cl₄F₁₂ requires C, 24·6; Cl, 29·0%), b. p. 203—205°/744 mm. (Siwoloboff), a colourless oil which showed no i.r. absorption in the double-bond region.

(b) Oxidation. Perfluoro(tricyclo[5,2,1,0^{2,6}]deca-3,8-

diene (0·1833 g., 0·527 mmoles) in acetone (5 ml.) was titrated against potassium permanganate (1·0522 g., 6·66 mmoles) in acetone (100·0 ml.); the titre (16·0 ml.; 1·07 mmoles $\equiv 2.03$ double bonds) confirmed ¹⁶ the dienic nature of the fluorocarbon.

(c) Pyrolysis. (i) Static pyrolysis. Perfluorocyclopentadiene dimer (0.35 g.) was recovered almost quantitatively after being heated at 475° for 45 min. in a 10×1 cm. platinum thimble encased in a silica ampoule; a further sample (0.05 g.) was completely decomposed to unidentified products after being heated similarly at 540° for 30 min.

(ii) Flow pyrolysis in platinum or silica. Perfluorocyclopentadiene dimer (6.70 g., 19.26 mmoles) was sublimed at 2 mm. pressure into a 100×1 cm. platinum tube which was heated to 650-660° over 56 cm. of its length; the contact time was 0.3 sec. The product, collected in two traps at -196° , was fractionated to provide tetrafluoroethylene (0.248 g., 2.48 mmoles; 36% yield based on starting material consumed), perfluorocyclopentadiene (0.741 g., 4.26 mmoles; 16%), and a mixture which was shown by g.l.c. analysis [2 m. di-(2-ethylhexyl)sebacate-Celite, 52°] to contain perfluorocyclopentadiene dimer (1.91 g., 5.47 mmoles; 29% recovery) and at least three other components. From this mixture was isolated, by g.l.c. (8 m. silicone oil-Celite, 130°), perfluoro(bicyclo[4,3,0]nona-2,4,7-triene) (1.65 g., 5.43 mmoles; 36%) (Found: C, 36.1. C_9F_{10} requires C, $36\cdot2\%$), b. p. $129^{\circ}/774$ mm. (Siwoloboff), $n_{\rm p}^{17\cdot5}$ 1.3719, with the mass spectrum listed in Table 3.

TABLE 3

Mass spectral data for perfluoro(bicyclo[4,3,0]nona-2,4,7-triene)

			,		
	Assign-	Abund-		Assign-	Abund-
m e	ment	ance	m e	ment	ance
31	CF^+	100.0	155	$C_{5}F_{5}^{+}$	1.7
69	CF_{3}^{+}	9.2	160	$C_{7}F_{4}^{+}$	$3 \cdot 4$
74	$C_3 \tilde{F}_2^+$	1.3	174	$C_5F_6^+$	$2 \cdot 3$
79	C_5F^+	1.8	179	$C_{7}F_{5}^{+}$	17.6
93	$C_3F_3^+$	12.3	186	$C_6F_6^+$	$6 \cdot 9$
98	$C_{5}F_{2}^{+}$	1.6	198	$C_{7}F_{6}^{+}$	$8 \cdot 3$
105	$C_{4}F_{8}^{+}$	1.7	210	$C_8F_6^+$	13.4
112	$C_{3}F_{4}^{+}$	20.9	217	$C_{7}F_{7}^{+}$	14.7
117	$C_{5}F_{3}^{+}$	10.9	229	$C_{8}F_{7}^{+}$	$22 \cdot 6$
122	$C_{7}F_{2}^{+}$	$1 \cdot 3$	241	$C_9F_7^+$	9·4
124	$C_4F_4^+$	$2 \cdot 6$	248	$C_8F_8^+$	$34 \cdot 1$
129	$C_{6}F_{3}^{+}$	1.6	260	$C_9F_8^+$	3.4
131	$C_3F_5^+$	$3 \cdot 9$	279	$C_9F_9^+$	16.5
141	$C_{7}F_{3}^{+}$	4.7	298	$C_{9}F_{10}^{+}$	38.0
148	C.F.+	1.5			

The products from a similar pyrolysis of perfluorocyclopentadiene dimer (11.85 g., 34.0 mmoles) at $680^{\circ}/2 \text{ mm}$. (contact time 0.3 sec.) were: tetrafluoroethylene (4.88 mmoles; 38% based on starting material consumed), perfluorocyclopentadiene (11.38 mmoles; 22%), unchanged starting

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material (8.30 mmoles; 24% recovery), perfluoro(bicyclo-[4,3,0]nona-2,4,7-triene) (10.27 mmoles; 40%), and unidentified material (38% by wt.).

Three pyrolyses were carried out using a 100×1 cm. silica pyrolysis tube heated over 56 cm. of its length. The results were as follows: At $490^{\circ}/2-3$ mm., with a contact time of ca. 2 sec., the starting material (0.439 g.) was recovered in 99% yield (0.435 g.). At $555^{\circ}/2$ -3 mm., with a contact time of ca. 2 sec., 0.435 g. (1.250 mmoles) of perfluorocyclopentadiene dimer gave traces of tetrafluoroethylene, perfluorocyclopentadiene (0.115 mmole; 96% yield based on starting material consumed), and unchanged dimer (1.190 mmoles; 95% recovery). At 590°/2 mm., with a contact time of ca. 2 sec., perfluorocyclopentadiene dimer (0.524 g., 1.506 mmoles) was converted into a mixture of tetrafluoroethylene (0.05 mmole; 29% based on starting material consumed), silicon tetrafluoride (trace), perfluorocyclopentadiene (0.174 mmole; 25%), unchanged dimer (1.164 mmoles; 77% recovery), perfluoro(bicyclo[4,3,0]nona-2,4,7-triene) (0.091 mmole; 27%), and unidentified material (0.047 g.).

Reactions of Perfluoro(bicyclo[4,3,0]nona-2,4,7-triene).— (a) Chlorination. The triene (0.37 g., 1.24 mmoles) and chlorine (0.65 g., 9.15 mmoles), sealed in a Pyrex ampoule, were irradiated for 42 hr. with light from a 500-w Hanovia u.v. lamp placed 18 in. distant. The product was shaken with mercury, leaving 2,3,4,5,7,8-hexachlorodecafluorobicyclo[4,3,0]nonane (0.62 g., 1.21 mmoles; 98%) (Found: C, 21.1. C₉Cl₆F₁₀ requires C, 21.1%), $n_{\rm D}^{20}$ 1.4463, a colourless liquid which showed no i.r. absorption in the ·C=C· region.

(b) Pyrolysis over iron. Perfluoro(bicyclo[4,3,0]nona-2,4,7-triene) (1.40 g., 4.70 mmoles) was dripped into the mouth of a 112 $\,\times\,$ 1·7 cm. mild steel tube which was packed with hydrogen-reduced (at 500°) mild steel wool, heated to 490-495° over 56 cm. of its length, and swept continuously with nitrogen (ca. 21./hr.); the contact time was ca. 4 min. The product, collected at -72° , was a golden-yellow liquid (1.05 g.) which was separated by g.l.c. (2 m. silicone oil-Celite analytical column, 57°) into the following materials: (i) Perfluoroindane (0.31 g., 1.04 mmoles; 28% yield based on starting material consumed) which had an unsatisfactory elemental analysis (Found: C, 38.5. Calc. for C₉F₁₀: C, 36.2%) but correct spectroscopic properties 13 [$\lambda_{max},$ 6.10(m), $\begin{array}{c} 6\cdot 56 \hspace{0.1cm} \mu \hspace{0.1cm} (vs) \hspace{0.1cm} ; \hspace{0.1cm} \lambda_{max} \hspace{0.1cm} (hexane) \hspace{0.1cm} 211 \hspace{0.1cm} (\epsilon \hspace{0.1cm} 5500) , \hspace{0.1cm} 267 \hspace{0.1cm} \overset{\text{max}}{\text{m}\mu} \hspace{0.1cm} (\epsilon \hspace{0.1cm} 900) , \\ \lambda_{\min} \hspace{0.1cm} 233 \hspace{0.1cm} \text{m}\mu \hspace{0.1cm} (\epsilon \hspace{0.1cm} 250) , \hspace{0.1cm} \lambda_{\inf} \hspace{0.1cm} 258 \\ - 260 \hspace{0.1cm} \text{m}\mu \hspace{0.1cm} (\epsilon \hspace{0.1cm} 740 \\ - 795) \hspace{0.1cm} ; \end{array}$ principal mass spectral peaks at m/e values of 298 (base peak due to parent ion, $C_9F_{10}^+$), 279 ($C_9F_9^+$, 44·1% abundance), 248 (C₈F₈⁺, 77.0%), 229 (C₈F₇⁺, 65.6%), 198 $(C_7F_6^+, 39.8\%)$, and 179 $(C_7F_5^+, 39.4\%)$]. (ii) Traces of a pale-yellow compound believed to be perfluoroindene (Found: C, 38.2%; M (mass spec.), 260. Calc. for C_9F_8 : C, 41.5%; M, 260). (iii) A mixture which gave two partially resolved g.l.c. peaks, one of which was due to the unchanged perfluoro(bicyclo[4,3,0]nona-2,4,7-triene) (estimated recovery 20%). The unidentified material showed i.r. absorptions at 5.8, 6.55, 6.6, 7.45, 7.65, 7.8, 9.65, 9.8, 11.75, and 12.4 µ.

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¹⁶ J. Burdon and J. C. Tatlow, J. Appl. Chem., 1958, 8, 293.