I. Chem. Soc. (C), 1967

## Polyfluorocyclopentadienes. Part III.<sup>1</sup> Diels-Alder Reactions of Perfluorocyclopentadiene<sup>2</sup>

#### By R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G. Orrell, The Chemistry Department, University of Manchester Institute of Science and Technology, Manchester 1

Perfluorocyclopentadiene partakes in the Diels-Alder reaction (a) as a diene in its thermal reactions with dimethyl acetylenedicarboxylate (----> dimethyl 1.2,3,4,7,7-hexafluorobicylo[2,2,1]hepta-2,5-diene-5,6-dicarboxylate), ethylene (----> 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene), acetylene (---> 1,2,3,4,7,7-hexafluorobicyclo-[2,2,1] hepta-2,5-diene), maleic anhydride (→→ 1,2,3,4,7,7-hexafluorobicyclo [2,2,1] hept-2-ene-5,6-anhydride), butadiene (→→ 1,2,3,4,7,7-hexafluoro-5-vinylbicyclo [2,2,1] hept-2-ene), norbornadiene (→→ two stereoisomers of 3,4,5,6,12,12-hexafluorotetracyclo[6,2,1,1<sup>3,6</sup>,0<sup>3,7</sup>]dodeca-4,9-diene), trifluoronitrosomethane {-----> perfluoro-(3-methyl-2-oxa-3-azabicyclo[2,2,1]hept-5-ene)}, but (b) as a dienophile when heated with anthracene [----> 9,10-dihydro-9,10-(11,12-hexafluorocyclopent-13-eno)anthracene], and (c) as both a diene (---->cyclo [5,2,1,0<sup>2,6</sup>] deca-3,8-diene) in its reaction with cyclopentadiene. The structures of the Diels-Alder adducts were determined by a combination of chemical and spectroscopic methods; the n.m.r. spectra of the adducts are discussed in detail, and a correlation between structure and <sup>19</sup>F n.m.r. spectral parameters is presented. No Diels-Alder adducts were obtained when perfluorocyclopentadiene was heated with tetracyanoethylene, tetrafluoroethylene, perfluorobutadiene, perchlorocyclopentadiene, or perchlorobutadiene.

Pyrolysis of dimethyl 1,2,3,4,7,7-hexafluoro[2,2,1]hepta-2,5-diene-5,6-dicarboxylate gave dimethyl tetrafluorophthalate and difluorocarbene, which was trapped with cyclohexene. Pyrolysis of perfluoro-(3-methyl-2-oxa-3-azabicyclo[2,2,1]hept-5-ene) was investigated, and its fluorination with cobalt trifluoride gave a compound believed to be perfluoro-(3-methyl-2-oxa-3-azabicyclo[2,2,1]heptane).

PERFLUOROCYCLOPENTADIENE,<sup>3</sup> which readily dimerises in Diels-Alder fashion to give perfluoro(tricyclo-[5,2,1,0<sup>2,6</sup>]deca-3,8-diene) (I),<sup>1,3</sup> partakes in the Diels-Alder reaction (a) as a diene in its thermal reactions with dimethyl acetylenedicarboxylate, ethylene, acetylene, maleic anhydride, butadiene, norbornadiene, or trifluoronitrosomethane, but (b) as a dienophile when heated with anthracene, and (c) as both a diene and a dienophile when treated with cyclopentadiene; even under forcing conditions it does not react with tetracyanoethylene, tetrafluoroethylene, perfluorobutadiene, perchlorobutadiene, or perchlorocyclopentadiene. Several other perfluoro-1,3-dienes combine with tri-

- <sup>2</sup> Preliminary communications, R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G. Orrell, Chem. Comm., 1965, 41; R. E. Banks, A. C. Harrison, and R. N. Haszeldine, ibid.,
- 1966, 338. <sup>3</sup> R. E. Banks, R. N. Haszeldine, and J. B. Walton, J. Chem.
- Soc., 1963, 5581. <sup>4</sup> R. E. Banks, M. G. Barlow, and R. N. Haszeldine, J. Chem. Soc., 1965, 6149.

fluoronitrosomethane or pentafluoronitrosobenzene to give what are formally Diels-Alder adducts [perfluorobuta-1,3-diene  $\longrightarrow$  (II); <sup>4</sup> perfluoro-(1,2-dimethylenecyclobutane)  $\longrightarrow$  (III) or (IV); <sup>5, 6</sup> perfluorocyclohexa-1,3-diene  $\longrightarrow$  (V) <sup>7</sup>], but only perfluorocyclohexa-1,3-diene has also been shown to enter into Diels-Alder reactions with hydrocarbon monoenes or dienes.<sup>8</sup> Perfluorobuta-1,3-diene, which gives,9 inter alia, the saturated tricyclic dimer (VI) and not perfluoro(vinylcyclohexene) when heated, has been treated with several conventional Diels-Alder dienes or dienophiles; but either no reaction has occurred (e.g., with maleic anhydride) or adducts believed to be cyclobutane deriva-

- <sup>5</sup> R. E. Banks, R. N. Haszeldine, and D. R. Taylor, J. Chem.
- Soc., 1965, 978. <sup>6</sup> R. E. Banks, W. R. Deem, R. N. Haszeldine, and D. R. Taylor, unpublished results.
- R. E. Banks, R. N. Haszeldine, and V. Matthews, unpublished results.
- <sup>8</sup> R. D. Chambers, W. K. R. Musgrave, and D. A. Pyke, Chem. and Ind., 1965, 564.
- <sup>9</sup> I. L. Karle, J. Karle, T. B. Owen, R. W. Broge, A. H. Fox, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1964, 86, 2523.

<sup>&</sup>lt;sup>1</sup> Part II, R. E. Banks, A. C. Harrison, and R. N. Haszeldine, J. Chem. Soc. (C), 1966, 2102.

tives [e.g., butadiene  $\longrightarrow$  (VII); acrylonitrile  $\longrightarrow$ (VIII)] have been isolated.<sup>10</sup> Reaction of perfluorobutadiene with tetrafluoroethylene yields perfluoro-(vinylcyclobutane) (IX).<sup>11</sup> Perfluoro-(1,2-dimethylenecyclobutane) undergoes thermal dimerisation to a compound believed to have structure (X),<sup>6</sup> and its reactions with conventional Diels-Alder dienes and dienophiles are under investigation.6



<sup>19</sup>F Nuclear Magnetic Resonance Spectra of the Diels-Alder Adducts from Perfluorocyclopentadiene.-The structures of the Diels-Alder adducts from perfluorocyclopentadiene were established by a combination of chemical and spectroscopic methods. At the outset, the interpretation of the high-resolution 60 Mc./sec. <sup>1</sup>H and 56.46 Mc./sec. <sup>19</sup>F n.m.r. spectra posed many difficulties, the chief of which was the absence of <sup>19</sup>F chemical shift data for the types of ring systems involved; also the complexities of the molecular structures made difficult the interpretation of spin-spin splittings. The basic problem was how to distinguish, by <sup>19</sup>F n.m.r. spectroscopy, between compounds containing a dienic residue (A), *i.e.*, arising from 1,4-addition to perfluorocyclopentadiene, and those containing a dienophilic residue (B), i.e., arising from 1,2-addition to perfluorocyclopentadiene.

This problem was solved by studying the spectrum of perfluorocyclopentadiene (see Experimental section) and those of its Diels-Alder adducts for which convincing structural evidence had been obtained by chemical or other spectroscopic (i.r., u.v., or mass) means. Thus, it was found that an adduct (strictly implying a bi- or poly-cyclic compound) containing the element of structure (A) gives a <sup>19</sup>F absorption pattern with characteristic parameters easily distinguishable from those associated

## 1609

with the presence of a structure of type (B) (see Table 1). These characteristic parameters, which will be referred to frequently in the subsequent discussion, are as follows. (i) The AB pattern (or single band if the nuclei show chemical equivalence) due to the  $CF_2$  group of the type present in (A) is centred at about 60 p.p.m. to high field of external trifluoroacetic acid, whereas for a CF<sub>2</sub> group of the type present in (B) it occurs at about 30 p.p.m. (ii) The geminal coupling constant for the  $CF_2$  group in (A) is ca. 175 c./sec., whereas for the  $CF_2$  group in (B) it is ca. 250 c./sec. The value of the internal chemical shift between the geminal fluorine nuclei does not appear to be a reliable parameter for distinguishing between (A) and (B) since it seems to depend on the overall molecular geometry. (iii) The tertiary fluorines in a compound containing structure (A) absorb at a much higher applied field (ca. 130 p.p.m.) than those in a compound of structure (B), and a considerable chemical shift difference is observed between type  $>CF \cdot CF_2$  and  $>CF \cdot CF$ .

The thermal dimer of perfluorocyclopentadiene (I), for which convincing structural proof was obtained other than by taking <sup>19</sup>F n.m.r. measurements,<sup>1</sup> contains both structural element (A) and (B); accordingly, its <sup>19</sup>F n.m.r. spectrum shows all the characteristic parameters referred to above,<sup>1,12</sup> e.g., two AB patterns centred at 32.2 and 52.4 p.p.m. to high field of trifluoroacetic acid, the  $|J_{gem}|$  values being 263 and 182 c./sec., respectively.

Reactions of Perfluorocyclopentadiene.—(a) With dimethyl acetylenedicarboxylate. Perfluorocyclopentadiene reacts with dimethyl acetylenedicarboxylate at 133° under autogenous pressure to give a 22% yield of a colourless, crystalline solid, m. p. 49-50°, which, on the basis of elemental analysis and the spectroscopic and chemical evidence presented below, is formulated as dimethyl 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene-5,6-dicarboxylate (XI). This Diels-Alder adduct is accompanied by much perfluorocyclopentadiene dimer (I) (50% yield), formation of which often seriously reduces the yields of the adducts sought in Diels-Alder reactions of perfluorocyclopentadiene.



Two plausible structures, (XI) and (XXII), can be written for the adduct, which gave only one peak when examined by g.l.c.; but pyrolysis experiments neatly provided powerful evidence in support of (XI) as the exclusive or predominant structure. Thermolysis of

<sup>&</sup>lt;sup>10</sup> R. M. Ryazanova, I. M. Dolgopol'skii, and A. L. Klebanskii, Zhur. Vsesoyuz. Khim. obshch. im D.Z. Mendeleeva, 1961, 6, 356.

<sup>&</sup>lt;sup>11</sup> R. E. Putnam, J. L. Anderson, and W. H. Sharkey, J. Amer. Chem. Soc., 1961, 83, 386. <sup>12</sup> R. Fields, M. Green, and A. Jones, J. Chem. Soc. (B), 1967,

<sup>270.</sup> 

# J. Chem. Soc. (C), 1967

## TABLE 1

<sup>19</sup>F N.m.r. (56·46 Mc./sec.) spectral parameters of Diels-Alder adducts of perfluorocyclopentadiene

		Chemical shift assignments (p.p.m. to high field of CF.CO.H)						
	Adduct	-CF <sub>2</sub> -	=CF-CF <	=CF-CF <sub>2</sub> -	≽cf	<i>J</i> <sub>gem</sub>   (c./sec.)		
(XI)	$F = F = CO_2 Me$ $F = F = CO_2 Me$	56.2	76.8		133.6	a		
(XII)	$F_{F} \xrightarrow{F}_{F_{1}}$	68·3	81.9	_	130.4	177		
(XIII)	F F F F	58·0	80.2	_	132.4	b		
(XIV)	$F = \begin{bmatrix} F \\ CO_2 H \\ F \end{bmatrix} = \begin{bmatrix} CO_2 H \\ CO_2 H \end{bmatrix}$	62-8	72.3		130.0	175		
(XVI)	$F = F_{F_2} CH: CH_2$	65.4	75·4 81·8	-	129·4 131·4	180		
(XVII)	$ \begin{array}{c} F \\ F \\ F \\ F \\ F \end{array} \qquad \qquad$	59·0 57·4	71·5 69·8	_	126·9 125·4	175 175		
(XVIII)	F = F = F	65-0	70·5 77·1		95·4 107·2	172		
(XIX)	F F F F	61-4	75·4 76·4		128.8	179		
(XX)	$\overbrace{F_{F_2}}^{F} \stackrel{F}{F_2}$	37.3		66.3, 75.4, 95.3, 103.8		260		
(XXI)	F F F2	32-1		66.7, 73.0, 85.8, 96.2		248		

The 56.2 p.p.m. band is basically a singlet, indicating chemical shift equivalence of the CF<sub>2</sub> fluorines.
The outer members of the basic AB quartet were not detected.
Obtained by hydrolysis of the adduct (XV).



#### Org.

the adduct at 480° in a sealed vessel gave dimethyl tetrafluorophthalate (34% yield), perfluorocyclobutane (35%), based on the annexed Scheme), and a trace of tetrafluoroethylene; that this decomposition involved the production of diffuorocarbene was proved by carrying out a similar pyrolysis in the presence of an excess of cyclohexene, when the only products identified were 7,7-difluoronorcarane (57% yield after g.l.c. isolation) and dimethyl tetrafluorophthalate. The Diels-Alder adduct of 5,5-difluorotetrachlorocyclopentadiene with dimethyl acetylenedicarboxylate also loses its difluoromethylene bridge when pyrolysed, and is thereby converted into dimethyl tetrachlorophthalate in 83%yield; 13 however, no attempt appears to have been made to discover the fate of the bridge. Tetramethoxyethylene and 1,2,3,4-tetrachlorobenzenes are formed when 1,2,3,4-tetrachloro-7,7-dimethoxybicyclo[2,2,1]hepta-

2,5-dienes are subjected to thermal decomposition; <sup>14</sup> presumably dimethoxycarbene is released and then dimerises.



The mass spectrum of the adduct was consistent with structure (XI). A weak molecular ion occurred, and also a low-intensity peak corresponding to the ion  $C_5F_6^+$ , attributable to the occurrence of a retro-Diels-Alder cleavage not observed when the adduct was pyrolysed. The base peak corresponded to an ion formed by cleavage of a methoxyl group from an aromatic ion arising from loss of the diffuoromethylene bridge from the molecular ion:



The i.r. spectrum of the adduct revealed the presence of both a  $\cdot$ CF:CF $\cdot$  and a  $\geq$ C:C $\leq$  group.

The <sup>19</sup>F n.m.r. spectrum of a 10% solution of the adduct in acetone consisted of three absorption regions of equal relative intensities at 56.2, 76.8, and 133.6 p.p.m. to high field of external trifluoroacetic acid. The <sup>13</sup> E. T. McBee, D. K. Smith, and H. E. Ungnade, J. Amer. Chem. Soc., 1955, 77, 387.

simplicity of the spectrum, which showed no impurity bands, is consistent with structure (XI), and, taken in conjunction with the pyrolysis and mass spectral data, leads us to reject structure (XXII) or any other alternative structure to that of dimethyl 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene-5,6-dicarboxylate

(XI). The 56.2 p.p.m. n.m.r. band, basically a singlet due to equivalence of the nuclei, is assigned to the geminal fluorines by comparison with the spectrum of perfluorocyclopentadiene ( $\delta_{CF_1} = 61.2$  p.p.m.), while the 76.8 p.p.m. absorption, which had a seven-line multiplet structure that was not examined, is assigned to the vinylic fluorines. The band at 133.6 p.p.m., a 1:2:1 triplet, is assigned to the tertiary fluorines.

(b) With ethylene. Reaction of perfluorocyclopentadiene with an excess of ethylene in a sealed tube at 106° gives 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (XII) in 51% yield, together with perfluorocyclopentadiene dimer (I) in 41% yield. The adduct (XII) shows a strong  $\cdot$ CF=CF $\cdot$  stretching frequency at 5.70  $\mu$  in the i.r., and its <sup>19</sup>F n.m.r. spectrum (see Table 1) is characteristic of a bicyclic compound containing the element of structure (A); its <sup>1</sup>H n.m.r. spectrum consists of a single complex region of absorption centred at  $\tau$  7.75, as expected for a symmetrical molecule containing only methylene protons adjacent to a >CF- group. The mass spectrum of the adduct shows a strong molecular ion and the base peak corresponds to the ion  $C_6H_4F_3^+$ ; the molecular ion degrades (a) by loss of diffuorocarbene and (b) by a Diels-Alder retrogression:



(c) With acetylene. Perfluorocyclopentadiene reacts with an excess of acetylene at  $115^{\circ}/ca$ . 12 atmospheres to give 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene (XIII) (42% yield) and perfluorocyclopentadiene dimer (I) (22%); the former product shows two olefinic absorptions in the i.r. (•CF:CF• and •CH:CH• str.) and gives a <sup>19</sup>F n.m.r. spectrum in keeping with the structure assigned (see Table 1). The <sup>1</sup>H n.m.r. spectrum of (XIII) is a single complex absorption centred at  $\tau$  3.25. The base peak in the mass spectrum of (XIII) corresponds to the ion C<sub>6</sub>H<sub>2</sub>F<sub>4</sub><sup>+</sup>, arising through loss of difluorocarbene from the molecular ion C<sub>7</sub>H<sub>2</sub>F<sub>6</sub><sup>+</sup>, which is the second

<sup>&</sup>lt;sup>14</sup> R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 1964, 197; D. M. Lemal, E. P. Gosselink, and A. Ault, *ibid.*, p. 579; R. W. Hoffmann and H. Häuser, *Angew. Chem. Internat. Edn.*, 1964, **3**, 380.

most abundant ion; as with the ethylene adduct (XII), the molecular ion also breaks down *via* a retro-Diels-Alder cleavage.

(d) With maleic anhydride. 1,2,3,4,7,7-Hexafluorobicyclo[2,2,1]hept-2-ene-5,6-anhydride (XV) (41% yield) and perfluorocyclopentadiene dimer (53%) were obtained when perfluorocyclopentadiene was heated with maleic anhydride at 110°. The Diels-Alder adduct (XV) showed characteristic absorptions in the i.r. at 5.36, 5.63 (anhydride group), and 5.73  $\mu$  (·CF=CF· str.; mull), and hydrolysed readily to the parent acid (XIV). The latter gave a <sup>19</sup>F n.m.r. spectrum of the correct type (see Table 1); only five absorptions were present, four of which were incorporated in the AB pattern centred at 62.8 p.p.m.  $[|J_{gem}| = 175 \text{ c./sec.}; (v_0 \delta) = 21.2 \text{ p.p.m.}].$  The  $72 \cdot 3$  p.p.m. band assigned to the vinylic fluorines was superimposed upon one of the high-field components of the AB system, and the final band at 130.0 p.p.m. was due to the tertiary fluorines. The fact that only single bands were given by the vinylic and tertiary fluorines is consistent with the symmetrical structure assigned to di-acid (XIV) and hence the anhydride adduct (XV). An attempt to decarboxylate the di-acid with soda-lime at temperatures up to 300° resulted in the formation of perfluorocyclopentadiene (29%) and its dimer (33%).

It is not known whether adduct (XV) has an *endo* or an *exo* configuration.



(e) With butadiene. Reaction of perfluorocyclopentadiene with an equimolar amount of butadiene at  $100^{\circ}$ under autogenous pressure yields perfluorocyclopentadiene dimer (25%) and both a 1:1 and a 2:1 Diels-Alder adduct (64 and <1% yield, respectively), to which are assigned structures (XVI) and (XXIII).

The presence of a vinyl substituent in the 1:1 adduct, a colourless liquid, b. p. 132°, showing both fluorocarbon and hydrocarbon olefinic bands in the i.r., was established by ozonolysis, which provided formaldehyde in at least 11% yield, and was fully confirmed by <sup>1</sup>H n.m.r. spectroscopy. Indeed, the latter technique revealed that, despite the low yield of formaldehyde, the adduct consisted solely of material containing a vinyl group [*i.e.*, (XVI), (XXV), or (XXVI)] and so enabled structure (XXIV) to be ruled out. The 60 Mc./sec. <sup>1</sup>H n.m.r. spectrum of the adduct consisted of two main absorption regions of relative intensities 1.0:1.0; the low-field region, centred at  $\tau$  4.45, was complex and typical of vinyl groups; the high-field region was in three main parts, a complex multi-<sup>15</sup> D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S.

Raasch, J. Amer. Chem. Soc., 1949, 71, 490.

plet at  $\tau$  6.70, assigned to a tertiary hydrogen, and complex absorptions at  $\tau$  7.45 and  $\tau$  8.05 which are assigned to two non-equivalent methylene protons. The spectrum is incompatible with structure (XXIV), which would give rise to two proton absorption regions of relative intensities 2.0: 1.0 due to the four methylene protons and the two vinylic protons, respectively. Support for the above analysis was provided by comparison of the fine structure pattern of the spectrum of the adduct with that of the <sup>1</sup>H spectrum of the vinylcyclobutane (XXVII), obtained in 97% yield by heating tetrafluoroethylene with butadiene; <sup>15</sup> the spectra were very similar, particularly in the vinyl absorption region, which was centred at  $\tau$  4.45 for both compounds.

Distinction between structure (XVI) and (XXV) or (XXVI) was made on the basis of the <sup>19</sup>F n.m.r. spectrum of the 1 : 1 adduct (see Table 1), which consisted of eight absorption lines. Four of these formed an AB pattern centred at 65.4 p.p.m.  $[|J_{gem}| = 180 \text{ c./sec.}; (v_0\delta) = 15.63 \text{ p.p.m.}]$  due to the CF<sub>2</sub> group in a residue of type (A).

The mass spectrum of (XVI) showed a relatively intense molecular ion, and the base peak resulted from the retro-Diels-Alder cleavage:



No attempt was made to determine whether adduct (XVI) possessed an *endo* or an *exo* configuration.

Since the l : l adduct of perfluorocyclopentadiene with butadiene was not, on the basis of the above evidence, allocated a cyclobutane structure [*i.e.*, (XXV) or (XXVI)], it was assumed that the 2 : l adduct, a white solid, m. p. 167—168°, was not a cyclobutane derivative either. Thus, consideration was given only to structures (XXIII), (XXVIII), and (XXIX), derived, respectively, from, (i) 1,4-addition of the l : l adduct (XVI) across perfluorocyclopentadiene, (ii) 1,4-addition across butadiene of the 8,9-double bond in perfluorocyclopentadiene dimer (I) (isolated in 25% yield from the reaction), and (iii) 1,4-addition across butadiene of the 3,4-double bond in perfluorocyclopentadiene dimer;



## 1613

Apart from an elemental analysis, the low yield (<1%) of the 2:1 adduct precluded structural investigations other than measurement of an i.r. spectrum, which showed only one olefinic band at 5.69  $\mu$ , assigned to a ·CF=CF· stretching mode, and contained no absorption near 6.0  $\mu$  typical of a ·CH=CH· group in compounds of type (XXVIII) or (XXIX). On this basis, structure (XXIII) is preferred for the 2:1 adduct.

(f) With norbornadiene. Reaction of perfluorocyclopentadiene with norbornadiene at  $100^{\circ}$  in a sealed tube gave a quantitative yield of a mixture of two stereoisomers of 3,4,5,6,12,12-hexafluorotetracyclo[6,2,1,1,<sup>3,6</sup>,0<sup>2,7</sup>]dodeca-4,9-diene (XVII C) and (XVII D), which were separated by g.l.c.



The above structural assignments are based mainly on the n.m.r. evidence discussed below, which differentiates between (XVII) and the other possible structures which must be considered, namely a nortricyclene structure [e.g., (XXX), which also has an *exo* form], since norbornadiene frequently yields nortricyclene derivatives when treated with powerful dienophiles,<sup>16</sup> and a cyclobutane derivative (XXXI), since tetrafluoroethylene reacts with norbornadiene to give compound (XXXII).<sup>17</sup>

Both adducts show a strong ·CF=CF· absorption near 5.7  $\mu$  and a weak ·CH=CH· absorption near 6.0  $\mu$ . The <sup>1</sup>H n.m.r. spectrum of isomer C has four regions of absorption each with the same relative intensity; a band at  $\tau$  3.70 is assigned to two vinylic protons, and bands at  $\tau$  7.02 and 7.44 to two types of tertiary protons, while an AB pattern  $[|J_{gem}| = 12.0 \text{ c./sec.}; (v_0\delta) = 0.31$ p.p.m.] centred at  $\tau$  8.40 is assigned to a methylene bridge. The less abundant isomer D has a similar spectrum, with three regions of absorption of relative intensities 1:2:1 at  $\tau$  values of 3.95, 6.97, and 8.40, which are assigned to vinylic, tertiary, and methylene protons, respectively; the absorption centred at  $\tau$  8.40 is an AB pattern  $[|J_{gem}| = 9.0 \text{ c./sec.}; (v_0 \delta) = 0.296$ p.p.m.], indicating that the methylene protons are non-equivalent.

The <sup>19</sup>F n.m.r. spectra of the two isomeric adducts

clearly shows (see Table 1) that both contain the element of structure (A) and therefore arise through 1,4-addition of one of the double bonds in norbornadiene across perfluorocyclopentadiene to give structure (XVII). Four stereoisomeric forms of (XVII) are possible, *viz., endo-endo endo-exo, exo-endo*, and *exo-exo*, and in order to attempt to determine whether (XVII C) or (XVII D) was the *endo-endo* isomer (XXXIII), hexane solutions of both isomers were separately irradiated with u.v. light to see if either would cyclise to a cage-like compound (XXXIV), like the chloro-analogue of (XXXIII).<sup>18</sup>



Isomer C was recovered quantitatively after irradiation for 1.5 days, but under identical conditions D was partly converted into a small amount of unidentified viscid material; thus, it seems that (XVII C) probably does not have the *endo-endo* configuration (XXXIII), while even



such a tentative conclusion cannot be applied to isomer (XVII D). Of the two isomers, (XVII D), being a reasonably high-melting solid, would be expected to be more likely to have the close-packed *endo-endo* configuration.

Although it is well-established <sup>19</sup> that the difference between coupling of endo  $(J \cong 0 \text{ c./sec.})$  and of exo  $(J = 3 \cdot 0 - 5 \cdot 0 \text{ c./sec.})$  protons with adjacent bridgehead hydrogens enables configurational assignments to be made in the norbornene and norbornane series, no use could be made of this to establish the absolute configurations of isomers (XVII C) and (XVII D), because the tertiary proton absorptions in their <sup>1</sup>H n.m.r. spectra were insufficiently resolved by the instrument used to enable  $J_{ab}$  and  $J_{cd}$  values to be determined.

(g) With trifluoronitrosomethane. Perfluorocyclopentadiene combines readily with trifluoronitrosomethane at room temperature to give a quantitative yield of a liquid 1:1 adduct, b. p. 61.8° the vapour of which shows an intense  $\cdot$ CF=CF $\cdot$  absorption in the i.r. at 5.72  $\mu$ . This adduct is formulated as perfluoro-(3-methyl-2-oxa-3-azabicyclo[2,2,1]hept-5-ene) (XVIII) mainly on the basis of n.m.r. spectroscopic evidence (see Table 1).

Org.

<sup>&</sup>lt;sup>16</sup> E. F. Ullman, *Chem. and Ind.*, 1958, 1173; A. T. Blomquist and Y. C. Meinwald, *J. Amer. Chem. Soc.*, 1959, **81**, 667; C. G. Krespan, B. C. McKusick, and T. L. Cairns, *ibid.*, 1961, **83**, 3428; H. K. Hall, *J. Org. Chem.*, 1960, **25**, 42; S. J. Cristol, E. L. Allred, and D. L. Wetzl, *ibid.*, 1962, **27**, 4058; C. D. Weiss, *ibid.*, 1963, **28**, 74; R. C. Cookson, J. Dance, and J. Hudec, *J. Chem. Soc.*, 1964, 5416.

 <sup>&</sup>lt;sup>17</sup> W. R. Brasen, U.S. 2,928,865/1960; R. E. Putnam, unpublished work referred to in *J. Amer. Chem. Soc.*, 1961, 83, 1657.
 <sup>18</sup> R. C. Cookson and E. Crundwell, *Chem. and Ind.*, 1958, 1004.

<sup>&</sup>lt;sup>19</sup> P. Laszlo and P. von R. Schleyer, J. Amer. Chem. Soc., 1964, **86**, 1171.

Rigorous g.l.c. analysis of the adduct indicated that it was not a mixture of isomers.

The <sup>19</sup>F n.m.r. spectrum of the adduct consists of eight absorption regions, one of which is composed of two overlapping groups. A band at -6.6 p.p.m. (relative to  $CF_3 \cdot CO_2H$ ) is assigned to the  $CF_3$  group of (XVIII), and an AB system [ $|J_{gem}| = 172$  c./sec.;  $(v_0\delta) = 12.9$ p.p.m.] due to the presence of a difluoromethylene group of type (A) occurs at 65.0 p.p.m. Complex multiplet bands at 70.5 and 77.1 p.p.m. are assigned to the two vinylic fluorines. The two tertiary fluorines absorb at 95.4 and 107.2 p.p.m.; the latter is more likely to be due to the tertiary fluorine of the >CF·N(CF<sub>3</sub>)- group rather than of the >CF·O- group from consideration of the relative electronegativities and hence de-shielding effects of nitrogen and oxygen. The multiplet structures of the individual bands are complex and, in the case of some bands, poorly resolved, so they remain unanalysed. The rather low chemical-shift values of the tertiary fluorines relative to the values obtained for analogous nuclei in the other Diels-Alder adducts of type (A) (see Table 1) are expected in view of the presence of adjacent electronegative nitrogen or oxygen nuclei.

The mass spectrum of the adduct is consistent with structure (XVIII). It shows a low-intensity molecular ion, an intense peak due to  $CF_3^+$  and a base peak due to the  $C_5F_6^+$  ion provided by a retro-Diels-Alder cleavage; the other possible ion from such a cleavage,  $CF_3NO^+$ , also appears in the spectrum but is much less abundant than  $C_5F_6^+$ . The spectrum provides no evidence for the cleavage of the  $CF_2$  bridge from the molecular ion.

No reaction occurs, except decomposition of a small percentage of the nitroso-compound, when the adduct (XVIII) is heated with trifluoronitrosomethane at 100°.

The pyrolysis and the fluorination of the adduct were investigated briefly. Flow pyrolysis at  $580^{\circ}/3$  mm. in platinum with a contact time of *ca.* 1 sec. caused 82%decomposition of the adduct to occur, with formation of perfluorocyclopentadiene (69%), nitric oxide (51%), hexafluoroethane (10%), perfluoro(methylenemethylamine) (7%), carbonyl fluoride (3%), and traces of tetrafluoroethylene, trifluoromethyl isocyanate, carbon tetrafluoride, perfluorocyclobutane, nitrous oxide, and unidentified tar. The high yield of perfluorocyclopentadiene seems much more in keeping with structure (XVIII) than an oxazetidine-type structure like, for example, (XXXV), which would be expected <sup>20</sup> to decompose mainly in the following fashion:

Treatment of adduct (XVIII) with cobalt trifluoride under conditions similar to those which convert perfluoro-(3,6-dihydro-2-methyl-2H-1,2-oxazine) (II) into perfluoro(tetrahydro-2-methyl-2H-1,2-oxazine)

(XXXVI),<sup>7</sup> led to the isolation of a small amount of

material believed, on the basis of its molecular weight, i.r. spectrum, and mass spectrum, to be perfluoro-(3-methyl-2-oxa-3-azabicyclo[2,2,1]heptane) (XXXVII).

$$\begin{array}{ccccccc} F_{2} & F_{2} & F_{2} & F_{2} \\ F_{2} & F_{2} & F_{2} & 0 \\ (III) & (XXXVI) & F_{2} & F_{2} & F_{2} & 0 \\ \end{array}$$

(h) With anthracene. Reaction of perfluorocyclopentadiene with anthracene in toluene at  $120^{\circ}$  gave a 27% yield of a solid 1 : 1 adduct, troublesome to separate from unchanged anthracene and believed to be 9,10-dihydro-9,10-(11,12-hexafluorocyclopent-13-eno)anthracene (XXI) from its spectroscopic properties.



The four most plausible structures (XXI) and (XXXVIII)—(XL) for the 1:1 adduct include one (XXI) arising from a Diels-Alder reaction in which the anthracene has acted as the diene in conventional fashion, one (XXXVIII) arising from the assumption of the dienic rôle by perfluorocyclopentadiene, and two with incorporated cyclobutane rings; attack by electrondeficient perfluorocyclopentadiene at the 1,2-bond in anthracene, necessary for the formation of adducts (XXXVIII)— (XL), would be expected in view of the high bond-order in that position.

The i.r. spectrum of the adduct shows an intense olefinic band at 5.68  $\mu$  (·CF=CF· str.) and two strong absorptions at 13.08 and 13.22  $\mu$ , which are assigned to aromatic C-H out-of-plane deformations. The u.v. spectrum of a solution of the adduct in ethanol strongly supports structure (XXI), since it exhibits an *E*-band at 212 m $\mu$ ( $\varepsilon$  9900) and *B*-bands at 248 ( $\varepsilon$  650), 264 ( $\varepsilon$  610), and 272 m $\mu$  ( $\varepsilon$  596), which suggests the presence of auxochromically-substituted benzenoid nuclei. Compounds (XXXVIII)—(XL) contain a vinylnaphthalene system, which would be expected to exhibit intense *K*-bands in the 200—250 m $\mu$  ( $\varepsilon_{max}$  >10,000) region; further, they would be expected to show *B*-bands of greater intensity

<sup>20</sup> R. E. Banks, R. N. Haszeldine, H. Sutcliffe, and C. J. Willis, J. Chem. Soc., 1965, 2506, and references quoted therein.

and at longer wavelength than those observed for the adduct.

The <sup>1</sup>H n.m.r. spectrum of the perfluorocyclopentadiene-anthracene adduct, which was closely similar to that of the well-known<sup>21</sup> Diels-Alder adduct of maleic anhydride and anthracene, gave excellent support to the conclusion reached from the u.v. measurements; it consisted of two absorptions of relative intensities 4 : 1 centred, respectively, at  $\tau 2.73$ , an aromatic absorption of the AA'BB' type, and  $\tau$  5.27, a multiplet due to tertiary hydrogens. No absorption occurred in the region expected for vinylic hydrogens, as demanded by structures (XXXVIII)-(XL). The <sup>19</sup>F n.m.r. spectrum of the adduct (see Table 1) fully confirmed structure (XXI). It consisted of eight absorptions, four of which formed an AB pattern centred at  $32 \cdot 1$ p.p.m. to high-field of trifluoroacetic acid, which is assigned to the two non-equivalent fluorines of the CF<sub>2</sub> group  $[|J_{gem}| = 248 \text{ c./sec.}; (v_0 \delta) = 16.0 \text{ p.p.m.}];$  the individual components of the AB system exhibited complex splitting patterns, which have not been interpreted. The four remaining bands in the spectrum occur at 66.7, 73.0, 85.8, and 96.2 p.p.m., *i.e.*, in the region associated with vinylic and tertiary fluorine nuclei, but no individual assignments can be made with any certainty. It is clear that both the two vinylic and the two tertiary fluorines are non-equivalent, which strongly suggests that unsymmetrical addition of anthracene across the 1,2-positions of perfluorocyclopentadiene has occurred and provides extra support for the assignments of spectral parameters discussed earlier. The 1:1 adduct of perfluorocyclopentadiene and anthracene was the first containing the element of structure (B) to be encountered.

(i) With cyclopentadiene. Reaction of perfluorocyclopentadiene with an equimolar amount of cyclopentadiene at 120-125° for 4 days (an excessive reaction period) gives a quantitative yield of a 16 : 84 mixture of two 1 : 1 adducts, which, on the basis of n.m.r. measurements, are allocated structures (XIX) and (XX), presumed to have endo configurations; the latter adduct could not be separated from traces of a third product, which, from <sup>19</sup>F n.m.r. spectroscopy, is believed to be either a stereoisomer of (XX) or to have structure (XLI) or (XLII). The ratio of (XIX): (XX) in quantitative reactions between perfluorocyclopentadiene and cyclopentadiene is unaffected either by the use of polar solvents or by change in reaction temperature within the range in which the interconversion  $(XIX) \iff (XX)$  does not occur; the mechanistic implications of these facts have been discussed.<sup>2</sup>

The <sup>1</sup>H n.m.r. spectrum of the least abundant product (XIX) (measured on a *ca*. 10% solution in carbon tetrachloride) has four main absorption regions, namely, an AB-type band centred at  $\tau$  4·15, two broad bands at

# 1615

 $\tau$  6.28 and 6.75 and a single band at  $\tau$  7.52. The integrated intensities of these band systems are almost in the ratio 2:1:1:2, and are thus assigned, respectively, to the vinylic protons, which are apparently nonequivalent, a tertiary proton, another tertiary proton, and the methylene protons. The general form of the spectrum, particularly in the vinylic region, corresponds very closely to the <sup>1</sup>H spectra of compounds (XLIII) <sup>22</sup> and (XLIV) <sup>23</sup> which are structurally related to (XIX).



By contrast, the <sup>1</sup>H n.m.r. spectrum of the other adduct (XX) (measured on a *ca*. 10% solution in carbon tetrachloride) has a sharp signal at  $\tau$  3.85 (integrated intensity 2.00) assigned to the vinylic protons, a single rather broad band centred at  $\tau$  6.86 (integrated intensity 1.76) due to the tertiary protons, and an AB pattern  $[|J_{gem}| = 10.2 \text{ c./sec.}; (v_0\delta) = 0.29 \text{ p.p.m.}]$  (total integrated intensity 1.96) centred at  $\tau$  7.67, due to the methylene protons. The most revealing feature of the spectrum is the sharp band at  $\tau$  3.85, as expected for a norbornene derivative.<sup>19, 23</sup> Overall, the spectrum compares well with those of the related compounds (XLV) <sup>22</sup> and (XLVI).<sup>23</sup>

The <sup>19</sup>F n.m.r. spectra of ca. 10% solutions of adducts (XIX) and (XX) are fully consistent with their  ${}^{1}H$ n.m.r. spectra (see Table 1). The spectrum of (XIX) exhibits the parameters expected for a tricyclic compound [type (A)] obtained by 1,4-addition to perfluorocyclopentadiene; all seven absorption regions in the spectrum are rather broad and do not exhibit any multiplet splitting. The <sup>19</sup>F spectrum of adduct (XX) is of the type (B) assigned to polycyclic adducts arising from 1,2-addition to perfluorocyclopentadiene; it has eight absorptions, four of which comprise an AB pattern  $[|J_{gem}| = 260 \text{ c./sec., } (v_0 \delta) = 15.9 \text{ p.p.m.; cf. (XIX),}$  $|J_{gem}| = 179$  c./sec.,  $(v_0 \delta) = 8.8$  p.p.m.] centred at 37.3 p.p.m. [cf. (XIX), 61.4 p.p.m.] and are assigned to the fluorine nuclei of the CF<sub>2</sub> group; the lower field components of this pattern are further split into a doublet (|J| = 14.7 c./sec.) of doublets (|J| = 9.6 c./sec.) of doublets (|J| = 5.1 c./sec.) of doublets (|J| = 2.8 c./sec.), due to spin-spin interactions with the four other fluorine nuclei in the molecule. The high-field components of the AB pattern exhibit complex coupling of a basic triplet nature, but this is only partially resolved and has not been analysed further. The other four main absorptions in the spectrum occur at values expected for vinylic and tertiary fluorines, but cannot be assigned individually.

<sup>23</sup> P. D. Bartlett, L. K. Montgomery, and B. Seidel, J. Amer. Chem. Soc., 1964, **86**, 616.

<sup>&</sup>lt;sup>21</sup> A. Wassermann, "Diels-Alder Reactions," Elsevier, London, 1965.

<sup>&</sup>lt;sup>22</sup> J. Drysdale, W. W. Gilbert, H. K. Sinclair, and W. H. Sharkey, J. Amer. Chem. Soc., 1958, **80**, 3672.

(i) With tetracyanoethylene, tetrafluoroethylene, perfluorobutadiene, perchlorocyclopentadiene, or perchlorobutadiene. Even under forcing conditions (100-300° in sealed vessels) no adducts appeared to be formed from perfluorocyclopentadiene and tetracyanoethylene, tetrafluoroethylene, perfluorobutadiene, perchlorocyclopentadiene, or perchlorobutadiene; in each reaction studied only unchanged starting materials or their pyrolysis products were isolated.

Comparison of Reactions of Perfluorocyclopentadiene with those of Perfluorocyclopentene, Perfluorobutadiene, and Perchlorocyclopentadiene.-In contrast to perfluorocyclopentadiene, perfluorocyclopentene is recovered quantitatively after being heated with ethylene (240°) or acetylene (260°), or kept at room temperature in the presence of trifluoronitrosomethane. This is not surprising, since it is well-established that for acyclic fluoroolefins only those containing a  $CF_2 = C \leq \text{group form four-}$ membered ring compounds when heated alone or in the presence of other unsaturated compounds, 20,24,25 e.g.,



However, the inertness of perfluorocyclopentene towards unsaturated substrates which do combine readily or fairly readily with perfluorocyclopentadiene indicates that the double bonds in the latter do not react independently of each other, *i.e.*, they are conjugated in the full sense of the word. This provides indirect support for the formulation of products from reaction of the diene with ethylene, acetylene, or trifluoronitrosomethane as Diels-Alder adducts, and not as a cyclobutane, a cyclobutene, and an oxazetidine derivative, respectively.

The exclusive preference shown by perfluorobutadiene to yield cyclobutane derivatives and not six-membered ring compounds when treated with dienes or dienophiles well-known for their ability to participate in Diels-Alder reactions, is consistent <sup>10</sup> with the proposal <sup>26</sup> that the inductive effect of the fluorines in perfluorobutadiene tends to localise the double bonds, thus inhibiting conjugation between them. A more appealing reason is that, as indicated by a study of molecular models (Courtauld), steric interaction between fluorine substituents at C-1 and C-4 prevents perfluorobutadiene from adopting a planar *cisoid* conformation, so that it cannot readily partake in a Diels-Alder reaction.

Perfluorocyclopentadiene strongly resembles perchlorocyclopentadiene<sup>27</sup> with respect to its Diels-Alder re-

actions. Clear differences are: (i) perchlorocyclopentadiene does not react with trifluoronitrosomethane at temperatures up to 100°; (ii) only one stereoisomeric form (the insecticide Aldrin) of adduct (XLVII) is



formed when perchlorocyclopentadiene is heated with norbornadiene; and (iii) thermal reaction of perchlorocyclopentadiene with anthracene yields principally a 2:1 adduct (XLVIII), together with small amounts of products which may have structures (XLIX) and (L). By contrast with the reactions between perfluorocyclopentadiene and anthracene or cyclopentadiene, no firmly-established example exists of a Diels-Alder reaction in which perchlorocyclopentadiene exhibits dienophilic activity towards another olefin or diene.<sup>28</sup>

The generalisation (the Alder rule) that a Diels-Alder reaction is favoured when the diene contains electron-releasing substituents and the dienophile contains electron-attracting substituents is one of wide currency. However, a number of reactions are known which do not comply with this principle,29 and a kinetic investigation 30 of some Diels-Alder reactions involving perchlorocyclopentadiene, an electron-poor component, and a range of dienophilic components has clearly shown that the reverse of the Alder rule is equally true. Even in the absence of quantitative rate measurements, it is obvious that the Diels-Alder reactions of perfluorocyclopentadiene are also subject to an inverse electron-demand effect: the diene does not react with tetracyanoethylene. tetrafluoroethylene, perfluorobutadiene, perchlorocyclopentadiene, or perchlorobutadiene under forcing conditions, but combines readily and quantitatively with cyclopentadiene or norbornadiene at 110°; dimethyl acetylenedicarboxylate and maleic anhydride react much more slowly at this temperature, so that competition occurs between adduct formation (22-41%) and dimerisation of the perfluorocyclopentadiene. When an equimolar mixture of perfluorocyclopentadiene, perchlorocyclopentadiene, and maleic anhydride was heated at 110° in a sealed tube, the yields of the two adducts

- <sup>28</sup> R. Riemschneider, Bołyu-Kagaku, 1963, 28, 83.
   <sup>29</sup> R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry June 1997.
- of Alkenes," ed. S. Patai, Interscience, London, 1964, p. 739. J. Sauer and H. Wiest, Angew. Chem. Internat. Edn., 1962, 269

<sup>J. D. Roberts and C. M. Sharts, Org. Reactions, 1962, 12, 1.
R. E. Banks, "Fluorocarbons and their Derivatives,"</sup> <sup>26</sup> R. N. Haszeldine, J. Chem. Soc., 1952, 4423.
 <sup>27</sup> H. E. Ungnade and E. T. McBee, Chem. Rev., 1958, 58, 249.

(XV) and (LI), determined by hydrolysis of these anhydrides and isolation of the parent acids, was 36 and 58%, respectively. This result suggests that the reactivity of the fluoro-diene towards maleic anhydride does not differ markedly from that of the chloro-diene, but does not provide a quantitative comparison since the reaction was not performed under truly one-phase conditions; also, competitive dimerisation of perfluorocyclopentadiene occurred, and the isolation procedures for the acids may not have been equally efficient.



#### EXPERIMENTAL

Perfluorocyclopentadiene is volatile (b. p.  $28^{\circ}$ ) and susceptible to attack by moist air, so it was manipulated in a Pyrex vacuum system and stored therein at  $-196^{\circ}$  to prevent dimerisation; it was prepared by dechlorination of tetrachlorohexafluorocyclopentane obtained by fluorination of perchlorocyclopentene with cobalt trifluoride.<sup>1,3</sup> Perfluorocyclopentene was prepared by fluorination of perchlorocyclopentene with potassium fluoride; <sup>31</sup> and perfluorobutadiene was obtained by dechlorination of 1,2,3,4-tetrachlorohexafluorobutane, which was synthesised from commercial chlorotrifluoroethylene by a modified literature method.<sup>32</sup> All the other starting materials were either commercial samples, purified by standard techniques, or samples prepared and purified according to the literature.

Products were identified by molecular weight determination (Regnault's or Victor Meyer's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 21 with sodium chloride optics), u.v. spectroscopy (Unicam SP 700 spectrophotometer), n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 56.46 Mc./sec. for <sup>19</sup>F spectra, with trifluoroacetic acid as external reference, and at 60 Mc./sec., with tetramethylsilane as internal reference, for <sup>1</sup>H spectra; the operating temperature was 34.5°), mass spectrometry (A.E.I. MS/2H spectrometer with a resolution of 1 in 700), and g.l.c. (Perkin-Elmer Fraktometer model 116 for routine work; Griffin and George Gas-Density Balance model D6 for quantitative analyses; Wilkins Aerograph Autoprep model A700 for most of the preparative separations). The n.m.r. chemical shift data were not corrected to allow for differences in bulk diamagnetic susceptibilities, since it was assumed that such corrections would be small and, in any case, fairly constant for the series of compounds examined.

Diels-Alder Reactions of Perfluorocyclopentadiene.—(a) Dimethyl acetylenedicarboxylate. A mixture of perfluorocyclopentadiene (3.68 g., 21.2 mmoles) and dimethyl acetylenedicarboxylate (3.00 g., 21.1 mmoles) was heated at 133° for 3 days in a 50-ml. Dreadnought ampoule. The volatile product consisted of perfluorocyclopentadiene dimer (1.84 g., 5.3 mmoles, 50% yield) and unidentified material absorbing in the i.r. at 3.3, 6.9, 7.4, 8.45, 9.35, and 12.6  $\mu$ . The involatile product, a golden-yellow viscous liquid, was extracted with light petroleum (b. p. 30—40°) (4 × 50 ml.); the extract was evaporated under reduced pressure to low volume (ca. 40 ml.), and the solid which precipitated was recrystallised thrice from light petroleum (b. p. 30—40°) to give dimethyl 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]*hepta*-2,5-*diene*-5,6-*dicarboxylate* (1·497 g., 4·7 mmoles; 22%) (Found: C, 41·8; H, 2·0.  $C_{11}H_6F_6O_4$  requires C, 41·8; H, 1·9%) as platelets, m. p. 49—50°,  $\lambda_{max.}$  (mull) 5·74 (C=O str.) with shoulder of nearly equal intensity at 5·71 (•CF=CF• str.), 6·08  $\mu$  (>C=C $\lt$  str.).

(b) With ethylene. A mixture of perfluorocyclopentadiene (2.60 g., 15.0 mmoles) and ethylene (1.398 g., 49.9 mmoles) in a 300-ml. Dreadnought ampoule was heated at 106° for 8 days. Fractionation of the product gave ethylene (1.160 g., 41.4 mmoles; 83% recovery) and a liquid (2.60 g.), which was separated by g.l.c. (2 m. Silicone MS550-Celite; 58°) into perfluorocyclopentadiene dimer (calculated yield 41%) and 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (calculated yield 51%) (Found: C, 41.5; H, 1.9.  $C_7H_4F_6$  requires C, 41.6; H, 2.0%), b. p. 107—108°/767 mm. (Siwoloboff),  $n_D^{22}$  1.3497,  $\lambda_{max}$  (film) 5.70  $\mu$  (•CF=CF• str.).

In a similar reaction at  $140^{\circ}$  during 4 days, perfluorocyclopentadiene (31.0 mmoles) and ethylene (31.0 mmoles) gave 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (18%; calculated by g.l.c. analysis) and perfluorocyclopentadiene dimer (80% by g.l.c.); while at 150° during 5.5 days, use of a 1.00: 1.55 molar reactant ratio provided these products in 24 and 73% yield, respectively.

(c) With acetylene (with D. W. ROBERTS). A mixture of perfluorocyclopentadiene (2.08 g., 12.0 mmoles) and acetylene (2.80 g., 0.108 mole) was heated at 115° for 65 hr. in a 200-ml. stainless-steel rocking autoclave. Fractionation of the volatile product gave perfluorocyclopentadiene dimer (0.24 g., 0.69 mmole, 12%) and a mixture (1.21 g.) which was shown by g.l.c. (4 m. silicone MS550-Celite; 120°), i.r., and n.m.r. analysis to contain perfluorocyclopentadiene dimer (ca. 0.2 g., 0.6 mmole, total yield ~22%) and 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene (ca. 1.0 g., 5.0 mmoles, ~42%),  $\lambda_{max}$ . 5.68s (·CF=CF· str.), 6.40w  $\mu$  (·CH=CH· str.). A pure sample of the diene (Found: C, 42.3; H, 1.5. C<sub>7</sub>H<sub>2</sub>F<sub>6</sub> requires C, 42.0; H, 1.0%) was isolated by g.l.c. (4 m. analytical Silicone MS550-Celite column; 120°).

(d) With maleic anhydride. (i) Alone. Under strictly anhydrous conditions, perfluorocyclopentadiene (0.85 g., 4.9 mmoles) and maleic anhydride (0.50 g., 5.1 mmoles) were heated together at 110° for 2 days in a 50-ml. Dreadnought tube. The volatile product was perfluorocyclopentadiene dimer (0.45 g., 1.3 mmoles, 53%) contaminated with a trace of perfluorocyclopentadiene. The solid product remaining in the reaction tube was sublimed at  $20^{\circ}/{<}1$  mm., to remove unchanged maleic anhydride (0.28 g., 2.86 mmoles, 56% recovery), m. p. 54°, mixed m. p. 53-54°, and the residue was sublimed at  $120^{\circ}/<1$  mm. to provide 1,2,3,4,7,7hexafluorobicyclo[2,2,1]hept-2-ene-5,6-anhydride (0.55 g., 2.0 mmoles; 41%) (Found: C, 39.9; H, 0.8.  $C_9H_2F_6O_3$ requires C, 39.7; H, 0.7%), m. p. 120–123°,  $\lambda_{max}$  (mull) 5.36, 5.63 (anhydride), 5.73 µ (·CF:CF· str.). Brief treatment of this new anhydride with hot water gave 1,2,3,4,7,7hexafluorobicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid (Found: C, 37.4; H, 1.5%; Equiv., 144. C<sub>9</sub>H<sub>4</sub>F<sub>6</sub>O<sub>4</sub> requires C, 37.2; H, 1.4%; Equiv., 145), isolated by standard techniques and purified either by sublimation at  $100-120^{\circ}/<1$  mm. or by recrystallisation from 1:1 (v/v) benzene-light petroleum (b. p. 30-40°), m. p. 164·0-

<sup>32</sup> R. N. Haszeldine, J. Chem. Soc., 1952, 4423; R. E. Banks, M. G. Barlow, R. N. Haszeldine, C. H. Thompson, and A. E. Tipping, publication in preparation; R. E. Banks, G. M. Haslam, R. N. Haszeldine, and A. Peppin, J. Chem. Soc. (C), 1966, 1171.

<sup>&</sup>lt;sup>31</sup> J. T. Maynard, J. Org. Chem., 1963, 28, 112.

## J. Chem. Soc. (C), 1967

165·5°,  $\lambda_{max.}$  (mull) 3·31 (broad, bonded OH), 5·70 ('CF=CF' str.), 5·85  $\mu$  (C=O str.).

(ii) In the presence of perchlorocyclopentadiene. A mixture of perfluorocyclopentadiene (0.65 g., 3.74 mmoles), maleic anhydride (0.367 g., 3.74 mmoles), and perchlorocyclopentadiene (1.02 g., 3.74 mmoles) was heated at 110° for 2 days in a 10-ml. Pyrex vial which was shaken occasionally. The volatile product was perfluorocyclopentadiene dimer (0.05 g., 0.14 mmoles, 8%) contaminated with traces of perfluorocyclopentadiene. The involatile product was heated under reflux with water (4 ml.) for 5 min., and the oil which separated from the cooled mixture was removed, washed with water (2 ml.), and cooled to 0°, when it solidified. The solid was recrystallised from toluene, to give 1,2,3,4,7,7hexachlorobicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid (0.806 g., 2.17 mmoles, 58%), m. p. and mixed m. p. 230-232°,  $\lambda_{max}$  2·8 (O–H str.), 5·75 (C=O str.), and 6·25  $\mu$  (·CCl=CCl- str.). The aqueous layer was evaporated to dryness and the white residue was sublimed at  $120^{\circ}/<1$ mm., to provide 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid (0.386 g., 1.35 mmoles, 36%), m. p. and mixed m. p. 162-163°, with correct i.r. spectrum.

(e) With butadiene. A mixture of perfluorocyclopentadiene (9.94 g., 56.7 mmoles) and butadiene (3.085 g., 57.1 mmoles) divided almost equally between two 300-ml. Dreadnought ampoules, was heated at 110° for 4.5 days. Butadiene (0.52 g., 9.6 mmoles, 17% recovery) was removed from the product, leaving a liquid containing a suspended solid; the solid was separated using a centrifuge, washed twice with diethyl ether (5 ml.), and recrystallised from acetone-water (40:60 v/v), to give 5,5'-bi-(1,2,3,4,7,7-hexafluorobicyclo[2,2,1]*hept-2-enyl*) (0.10 g., 0.25 mmole, <1%) (Found: C, 42.0; H, 1.8. C<sub>14</sub>H<sub>6</sub>F<sub>12</sub> requires C, 41.8; H, 1.5%), m. p. 167- $168^\circ\!,$  which, as a mull, showed only one olefinic absorption in the i.r. at 5.69  $\mu$  (CF=CF. str.). The liquid product was separated by g.l.c. (6 m.  $\times$  1.0 cm.; 20% w/w Silicone SE52-60/80 mesh Chromasorb W;  $122^{\circ}$ ; N<sub>2</sub> flow rate 300 ml./min.) into perfluorocyclopentadiene dimer (estimated yield 25%) and 1,2,3,4,7,7-hexafluoro-5-vinylbicyclo-[2,2,1]*hept-2-ene* (estimated yield 64%) (Found: C, 47·1; H, 2·6. C<sub>9</sub>H<sub>6</sub>F<sub>6</sub> requires C, 47·4; H, 2·6%), b. p. 132° (Siwoloboff),  $n_{\rm D}^{20}$  1·3813,  $\lambda_{\rm max}$  (film) 5·71s (·CF=CF· str.), 6·08s  $\mu$  (·CH=CH<sub>2</sub> str.). A small amount (<1 g.) of a transparent gel remained on the walls of the reaction tube; this showed i.r. absorptions at 3.4 (C-H str.), 5.78s (•CF=CF• str.), 6·12w (•CH=CH• str.), 7·38, and in the region 7.7—15.0  $\mu$  (continuous and indefinite), and may have contained a copolymer of perfluorocyclopentadiene with butadiene.

(f) With norbornadiene. A mixture of perfluorocyclopentadiene (8·15 g., 46·9 mmoles) and norbornadiene (4·40 g., 47·8 mmoles) was heated at 100° for 6 days in a 300-ml. Dreadnought ampoule. A volatile product (2·0 ml. at s.t.p.) was discarded, and the involatile liquid product was distilled in a semi-micro Vigreux still, to give 3,4,5,6,12,12-hexafluorotetracyclo[6,2,1,1<sup>3,6</sup>,0<sup>2,7</sup>]dodeca-4,9-diene (9·50 g., 35·7 mmoles, 76%) (Found: C, 54·1; H, 3·05.  $C_{12}H_8F_6$  requires C, 54·1; H, 3·0%), b. p. 110—114°/58 mm., and a stillpot residue (2·85 g.) of the same compound (total yield: 99%) containing (by g.l.c. analysis) ca. 2% of an unidentified impurity. The dodeca-4,9-diene was separated into two stereoisomeric forms (C and D) by g.l.c. (7·6 m. × 1·0 cm.; 30% w/w Apiezon L-Celite; 180°; N<sub>2</sub> flow rate 200 ml./ min.).

Isomer C (68% of the mixture; retention time 23.0 min.)

(Found: C, 53.9; H, 2.9.  $C_{12}H_8F_6$  requires C, 54.1; H, 3.0%) was a colourless liquid, b. p. 190°/772 mm. (Siwoloboff),  $n_D^{20.5}$  1.4255,  $\lambda_{max}$ . (film) 5.73s (·CF=CF· str.), 6.05w, 6.40w (one of these is a ·CH=CH· str.), 13.48s  $\mu$ .

Isomer D (32% of the mixture; retention time 29.0 min.) (Found: C, 54.1; H, 3.1.  $C_{12}H_8F_6$  requires C, 54.1; H, 3.0%) was a white solid, m. p. 98.5—101.0°,  $\lambda_{max}$  (mull) 5.73s (·CF=CF· str.), 5.97w, 6.37vw (one of these is a ·CH=CH· str.), 13.32  $\mu$ .

(g) With cyclopentadiene. A mixture of perfluorocyclopentadiene (8.85 g., 50.9 mmoles) and cyclopentadiene (3.36 g., 50.9 mmoles) was heated at  $120-125^{\circ}$  for 4 days. A trace (2 ml. at s.t.p.) of volatile product was not examined, but the liquid product was distilled in a semi-micro Vigreux still to provide a 16: 84 mixture (composition determined by g.l.c. analysis) of two isomeric Diels-Alder adducts (11.97 g., 49.8 mmoles, 98%) (Found: C, 50.2; H, 2.4. C<sub>10</sub>H<sub>6</sub>F<sub>6</sub> requires C, 50.0; H, 2.5%), b. p. 165-170°. The two adducts were separated by g.l.c. (6 m.  $\times$  1.0 cm.; 20% w/w Silicone SE52-60/80 mesh Chromasorb W; 150°;  $N_2$  flow rate 300 ml./min.), to provide 1,7,8,9,10,10-hexafluorotricyclo[5,2,1,0<sup>2,6</sup>]deca-3,8-diene (1.60 g., 6.67 mmoles, 13%) (Found: C, 50.0; H, 2.7. C<sub>10</sub>H<sub>6</sub>F<sub>6</sub> requires C, 50.0; H, 2.5%), a waxy solid, retention time 12.5 min., m. p. 37.0–39.5°,  $\lambda_{max}$  (melt) 5.71s (•CF=CF• str.), 6.17w  $\mu$ (•CH=CH• str.), and 2,3,4,5,5,6-hexafluorotricyclo[5,2,1,0<sup>2,6</sup>]deca-3,8-diene (8.40 g., 35.0 mmoles, 69%) (Found: C, 50.2; H, 2.3.  $C_{10}H_6F_6$  requires C, 50.0; H, 2.5%), a waxy solid, retention time 15.0 min., m. p. 23.0-25.0°,  $\lambda_{max}$  (melt) 5.70s (·CF=CF· str.), 6.01w µ (·CH=CH· str.), the chromatogram peak for which had a slight shoulder (at ca. 16.5 min. retention time) indicative of the presence of traces of impurity; the presence of ca. 1% of impurity in the second of the adducts was confirmed by <sup>19</sup>F n.m.r. spectroscopy.

(h) With trifluoronitrosomethane. A mixture of perfluorocyclopentadiene (2.88 g., 16.6 mmoles) and trifluoronitrosomethane (1.65 g., 16.7 mmoles) was left at room temperature overnight in a 300-ml. Dreadnought ampoule. The volatile product was fractionated, to yield trifluoronitrosomethane (0.2 mmole, 1% recovery) and perfluoro-(3-methyl-2-oxa-3-azabicyclo[2,2,1]hept-5-ene (4.42 g., 16.3 mmoles, 98%) (Found: C, 26.4; N, 5.2%; M, 273. C<sub>6</sub>F<sub>9</sub>NO requires C, 26.4; N, 5.1%; M, 273), b. p. 61.8° (isoteniscope),  $n_p^{21}$  1.3108, which gave only one peak on gas chromatograms (2 m., Silicone MS550-Celite at 20° or 4 m., Kel-F oil No. 10-Celite at 20°). A trace of viscous liquid was observed on the walls of the reaction vessel.

The vapour pressure of perfluoro-(3-methyl-2-oxa-3-aza-bicyclo[2,2,1]hept-5-ene), measured over the range  $0-60^{\circ}$ , is given by the equation  $\log_{10}p$  (cm.) =  $7\cdot02 - 1720/T$ , whence the b. p. is  $61\cdot8^{\circ}$ , Trouton's constant is  $23\cdot5$ , and the latent heat of vaporisation is 7880 cal. mole<sup>-1</sup>.

(i) With anthracene. A solution of perfluorocyclopentadiene (2·45 g., 14·1 mmoles) and anthracene (1·84 g., 10·3 mmoles) in sodium-dried toluene (10 ml.) was heated at 120° for 5 days in a 50-ml. Pyrex ampoule. The volatile product, identified by g.l.c. as a mixture of toluene and perfluorocyclopentadiene dimer, was removed from the ampoule, leaving a solid residue which was recrystallised twice from 40% aqueous ethanol to yield unchanged anthracene (0·78 g., 4·4 mmoles, 42% recovery), m. p. 215—217°, mixed m. p. 216—217°. The mother-liquors from the recrystallisations were treated with water, to precipitate a solid (1·40 g.) containing traces of anthracene (by i.r. analysis); unsuccessful attempts were made to remove the anthracene Published on 01 January 1967. Downloaded by Cornell University Library on 09/08/2016 10:24:14.

TABLE 2

Reaction of perfluorocyclopentadiene with tetrafluoroethylene

cyclo-C-F.	$C_2F_4$ (g.; mmoles)	Temp.	Time (hr.)	Products (mmoles; %)			
(g.; mmoles)				cyclo-C <sub>5</sub> F <sub>6</sub>	$(\text{cyclo-}C_5F_6)_2$	$C_2F_4$	cyclo-C <sub>4</sub> F <sub>8</sub>
4·25; 24·4	2.44; 24.4	100° a	60	1.4; 6	11.5; 94	24·2; 99	None
7.50; 43.1	4.30; 43.0	220 <sup>b</sup>	7	None	14.4; 79	28.4;66	<b>4</b> ·3; 20
4.10; 23.6	2.30; 23.0	300 <sup>b</sup>	9	None	0.3; 3	с	5.0; 43

<sup>a</sup> 300-ml. Dreadnought ampoule. <sup>b</sup> 100-ml. stainless-steel autoclave. <sup>c</sup> 188 ml. (at s.t.p.) of tetrafluoroethylene contaminated with silicon tetrafluoride (from attack on the vacuum system by the product) was isolated, and a deposit of carbonaceous material remained in the autoclave.

by fractional recrystallisation from aqueous ethanol, by fractional sublimation at ca. 0.5 mm. pressure, by liquidsolid chromatography on alumina type H using ethanol as eluent, and by zone-melting techniques. Finally, the following purification procedure had to be adopted. A sample of the solid (0.49 g.) was mixed with maleic anhydride (0.20 g.) and dissolved in xylene (10 ml.); the solution was heated under reflux for 10 min. then cooled to  $ca. 100^{\circ}$ and shaken with 4% sodium hydroxide solution (15 ml.). The xylene layer was separated, washed with water, dried  $(MgSO_4)$ , and distilled under reduced pressure to remove the xylene; the stillpot residue was recrystallised from 50% aqueous acetone and then sublimed at  $120^{\circ}/<1$  mm., to provide 9,10-dihydro-9,10-(11,12-hexafluorocyclopent-13-eno)anthracene (0.35 g.) (Found: C, 65.0; H, 2.9. C<sub>19</sub>H<sub>10</sub>F<sub>6</sub> requires C, 64.8; H, 2.8%), m. p. 145–147°,  $\lambda_{max.}$  (mull) 5.68 (·CF=CF· str.), 13.08, 13.22  $\mu$  (C-H def.),  $\lambda_{max}$  (ethanol) 212, 248, 264, 272, 300 m $\mu$  ( $\epsilon$  9900, 650, 610, 596, 59),  $\lambda_{\min}$  (ethanol) 245, 260, 268, 296 mµ ( $\varepsilon$  642, 560, 504, 50).

Unsuccessful Diels-Alder Reactions of Perfluorocyclopentadiene.—(a) With tetracyanoethylene. When a 2:1 molar mixture of perfluorocyclopentadiene and tetracyanoethylene in tetrahydrofuran was left at 20° for 10 days, the only products, isolated and identified by standard techniques, were tetrahydrofuran, perfluorocyclopentadiene and its dimer, and tetracyanoethylene (97% recovery).

When perfluorocyclopentadiene (1.00 g., 5.75 mmoles), tetracyanoethylene (0.75 g., 4.94 mmoles), and tetrahydrofuran (7 ml.) were heated together at 110° for 2.5 days in a 50-ml. Dreadnought ampoule, the volatile product consisted of tetrahydrofuran and perfluorocyclopentadiene dimer (0.72 g., 2.1 mmoles; 72%). A black residue from the reaction vessel was sublimed at 120°/ca. 0.5 mm., to give tetracyanoethylene (0.20 g., 1.3 mmoles, 27% recovery), and another black residue (0.73 g.) with an i.r. spectrum similar to those of black solids formed when tetracyanoethylene is heated alone for extended periods.<sup>33</sup>

(b) With tetrafluoroethylene. Table 2 gives the details of three experiments carried out by heating perfluorocyclopentadiene with tetrafluoroethylene in either a 300-ml. Dreadnought ampoule or a 100-ml. stainless steel autoclave.

(c) With perfluorobutadiene. A mixture of perfluorocyclopentadiene (3·10 g., 17·8 mmoles) and perfluorobutadiene (3·25 g., 20·1 mmoles) was heated at 230° for 17 hr. in a 300-ml. Dreadnought ampoule. A high-boiling liquid product (<0.1 g.), presumably oligomers of perfluorobutadiene, was not examined; the volatile product consisted of perfluorocyclobutene <sup>34</sup> (2·66 g., 16·4 mmoles, 82%) (Found: M, 163. Calc. for C<sub>4</sub>F<sub>6</sub>: M, 162) and perfluorocyclopentadiene dimer (3·10 g., 8·9 mmoles, 100%).

 $^{\mbox{\scriptsize 33}}$  J. M. Birchall, R. N. Haszeldine, and E. N. Taylor, personal communication.

(d) With perchlorobutadiene. A mixture of perfluorocyclopentadiene (0.20 g., 1.15 mmoles) and perchlorobutadiene (0.30 g., 1.15 mmoles) was heated at 220° for 2 days in a 20-ml. Pyrex tube. The product was separated by standard techniques into perfluorocyclopentadiene dimer (0.20 g., 0.57 mmoles, 100%) and perchlorobutadiene (0.30 g., 1.15 mmoles, 100%)

(e) With perchlorocyclopentadiene. A mixture of perfluorocyclopentadiene (0.97 g., 5.6 mmoles) and perchlorocyclopentadiene (1.53 g.; 5.6 mmoles), heated at 220° for 21 hr. in a 50-ml. Pyrex ampoule, gave perfluorocyclopentadiene dimer (0.96 g., 2.75 mmoles, 99%) and unchanged perchlorocyclopentadiene (1.51 g., 5.56 mmoles, 99%).

Reactions of the Diels-Alder Adducts from Perfluorocyclopentadiene.--(a) Pyrolysis of dimethyl 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene-5,6-dicarboxylate. (i) Alone. The ester (3.33 g. 10.55 mmoles), divided equally between two 400-ml. Pyrex ampoules, was heated at  $470-480^{\circ}$ for 30 min. The volatile product was fractionated, and the fractions were examined by standard methods and found to contain silicon tetrafluoride, carbon dioxide (3.09 mmoles), carbon tetrafluoride (<0.01 mmole), tetrafluoroethylene <1%), perfluorocyclobutane (0.187 g., (0.02 mmole)0.935 mmole, 35%), and unidentified material which gave only one peak on a gas chromatogram [8 m. Kel-F No. 10 oil-Celite; 22°; N<sub>2</sub> flow rate 40 ml./min.; corrected retention time 12.6 min. (cf. perfluorocyclobutane, 9.3 min.)]. The solid product was extracted with ether (4  $\times$  50 ml.) and the solid, golden-yellow residue was heated under reflux with light petroleum (b. p. 30-40°) (50 ml.) and animal charcoal (ca. 0.1 g.), and then recrystallised thrice from light petroleum (b. p. 30-40°), to provide dimethyl tetrafluorophthalate (0.946 g., 3.56 mmoles, 34%) (Found: C, 44.9; H, 2.5.  $C_{10}H_6F_4O_4$  requires C, 45.1; H, 2.3%), m. p. 71-73°,  $\lambda_{max}$  (mull) 5.78 (C=O str.), 6.61, and 6.76  $\mu$ (fluorinated aromatic nucleus),  $\lambda_{max}$  (ethanol) 276 m $\mu$  ( $\epsilon$  2030),  $\lambda_{min}$  255 m $\mu$  ( $\epsilon$  885),  $\lambda_{inff}$  217—222 ( $\epsilon$  7080—6650). A sample of dimethyl tetrafluorophthalate (0.354 g., 1.31 mmoles) was heated under reflux (24 hr.) with a mixture of water (15 ml.), concentrated hydrochloric acid (4 ml.), and rectified spirit (2 ml.); the hydrolysate was worked up to provide unchanged dimethyl tetrafluorophthalate (0.130 g., 0.49 mmole, 37% recovery), m. p. 71-73°, mixed m. p. 71-73°, and a solid (0.211 g.) which was sublimed at  $150^{\circ}/<1$  mm. to yield a mixture (0.060 g.) of tetrafluorophthalic acid and its anhydride (by i.r. spectroscopy). This mixture was converted into di-(S-benzylthiouronium) tetrafluorophthalate (0.150 g., 0.26 mmole, 31% based on dimethyl ester consumed) (Found: C, 50.6; H, 3.7; N, 9.7. Calc. for  $C_{24}H_{22}F_4N_4O_4S_2$ : C, 50.5; H,

<sup>34</sup> M. Prober and W. T. Miller, J. Amer. Chem. Soc., 1949, **71**, 598.

#### J. Chem. Soc. (C), 1967

**3.9;** N, **9.8%**), m. p. **204.5**—**205°** (decomp.), mixed m. p. **203.5**—**204.5°** (decomp.) [lit.,<sup>35</sup> **205°** (decomp.)].

(ii) In the presence of cyclohexene. A mixture of dimethyl 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene-5,6-dicarboxylate (1.65 g., 5.22 mmoles) and cyclohexene (1.76 g., 21.5 mmoles) was heated at 480° in a 300-ml. silica ampoule for 15 min. The volatile product was fractionated to give carbon dioxide (0.38 mmole), cyclohexene (0.31 mmole), and a binary mixture which was separated by g.l.c. (2 m., Silicone MS550-Celite; 86°; N<sub>2</sub> flow rate 60 ml./min.) into cyclohexene (1.10 g., 13.4 mmoles; 62%, total recovery 64%) and 7,7-difluoronorcarane (0.39 g., 2.95 mmoles, 57%), identified by comparison of its g.l.c. retention time and i.r. spectrum with those of an authentic sample. Dimethyl tetrafluorophthalate (0.88 g., 3.3 mmoles, 63%), m. p. 72-73°, was extracted from the residue in the reaction tube.

(b) Attempted decarboxylation of 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid. The di-acid (0.405 g., 1.41 mmoles) was mixed with soda-lime (1.063 g.) and heated slowly to 300°. A volatile product, collected in a trap at  $-72^{\circ}$ , consisted of perfluorocyclopentadiene (0.070 g., 0.40 mmole, 29%) and its dimer (0.082 g., 0.24 mmole, 33%).

(c) Ozonolysis of 1,2,3,4,7,7-hexafluoro-5-vinylbicyclo-[2,2,1]hept-2-ene. A slow stream of ozonised oxygen was bubbled through two Dreschel bottles in series, the first containing a solution of 1,2,3,4,7,7-hexafluoro-5-vinylbicyclo[2,2,1]hept-2-ene (0.784 g., 3.44 mmoles) in glacial acetic acid (50 ml.) and the second distilled water (50 ml.), until the exit gas gave a strong ozone test with starchiodide paper. The contents of the Drechsel bottles were steam distilled; the distillate (ca. 200 ml.) was neutralised with 40% aqueous sodium hydroxide, then made slightly acid with acetic acid, treated with dimedone (2 g.) in 50%aqueous ethanol (40 ml.), and left at  $ca. 5^{\circ}$  overnight. The precipitate was filtered off and recrystallised twice from aqueous ethanol, to provide the dimedone derivative of formaldehyde (0.113 g., 0.39 mmole, 11%), m. p. and mixed m. p. 187-188°.

(d) Attempted cyclisation of the isomers of 3,4,5,6,12,12hexafluorotetracyclo[ $6,2,1,1^{3,6},0^{2,7}$ ]dodeca-4,9-diene. (i) Isomer C. A solution of isomer C (b. p. 190°/772 mm.) (0.455 g., 1.71 mmoles) in hexane (10 ml.), contained in a 50-ml. silica ampoule, was irradiated for 38 hr. with u.v. light from a 500-w Hanovia lamp placed 21 cm. distant. Hexane was removed from the product *in vacuo*, leaving spectroscopically-pure (i.r.) isomer C (0.445 g., 1.68 mmoles, 98%).

(ii) Isomer D. A solution of D (m. p.  $98\cdot5-101\cdot0^{\circ}$ ) (0·306 g., 1·15 mmoles) in hexane (10 ml.), contained in a 50-ml. silica ampoule, was irradiated exactly as in (i) above. After removal of hexane from the product *in vacuo*, a waxy brown solid was obtained, which was shown by i.r. spectroscopy to contain isomer D and unknown material. The brown solid was oxidised with permanganate in acetone at 20° and the product was worked up to give traces of a gluelike product which absorbed strongly in the i.r. at 3·5, 7·35, 7·5, 10·65, and 10·7  $\mu$ .

In another experiment, a solution of isomer D (0.302 g.)in ethyl acetate (10 ml.) was irradiated exactly as described above, for 7 days. Removal of the solvent from the product, followed by vacuum sublimation of the viscous brown oil thus obtained, gave the same (by i.r. spectroscopy) gluelike material obtained when hexane was used as solvent.

(e) Reactions of perfluoro-(3-methyl-2-oxa-3-azabicyclo-[2,2,1] hept-5-ene). (i) Pyrolysis. The olefin  $(3.401 \text{ g}_{...})$ 12.46 mmoles) was vaporised from a trap cooled to  $-72^{\circ}$ and passed at 3 mm. pressure through a  $100 \times 1.0$  cm. platinum tube heated to 580° over 55 cm. of its length; the contact time was ca. 1 sec. The volatile product contained nitric oxide (5.20 mmoles; 51%), perfluoroethane (1.00 mmole; 10%), tetrafluoroethylene (0.07 mmole; 0.5%), carbonyl fluoride (0.33 mmole; 3%) perfluoro-(methylenemethylamine) (0.73 mmole; 7%), perfluorocyclopentadiene (7.06 mmoles; 69%), perfluoro-(3-methyl-2-oxa-3-azabicyclo[2,2,1]hept-5-ene) (2.30 mmoles; 18% recovery) and traces of trifluoromethyl isocyanate, carbon tetrafluoride, perfluorocyclobutane, silicon tetrafluoride, and nitrous oxide. An unidentified brown involatile product was formed in small amount.

(ii) With trifluoronitrosomethane. Perfluoro-(3-methyl-2-oxa-3-azabicyclo[2,2,1]hept-5-ene) (0.176 g., 0.646 mmole) and trifluoronitrosomethane (0.064 g., 0.646 mmole), heated at 100° for 21 hr. in a 300-ml. Pyrex ampoule, gave trifluoronitrosomethane (0.623 mmole; 96% recovery), unchanged bicyclo-compound (0.625 mmole, 97% recovery), and traces of carbon dioxide, silicon tetrafluoride, trifluoronitromethane, perfluoro(methylenemethylamine), and Onitrosobistrifluoromethylhydroxylamine.

(iii) Fluorination. Perfluoro-(3-methyl-2-oxa-3-azabicyclo-[2,2,1]hept-5-ene) (7.50 g., 27.5 mmoles) was vaporised and swept with a slow stream of nitrogen during 1.25 hr. through a  $24 \times 2$  in. static cobalt fluoride reactor containing cobalt trifluoride (300 g.). The liquid product (4.30 g.), trapped at  $-72^{\circ}$ , was shown by g.l.c. analysis [6 m., di-(2-ethylhexyl) sebacate-Celite; 22°; N<sub>2</sub> flow rate 50 ml./min.] to contain at least nine components. A small sample of the major component (retention time 3.0 min.), contaminated with olefinic material (i.r. band at 5.7  $\mu$ ), was trapped out, treated with a solution of potassium permanganate in acetone, recovered by standard techniques, subjected to trap-to-trap fractional condensation in vacuo and then subjected to molecular weight determination (Found: M, 298.  $C_6F_{11}$ NO requires M, 311) and examined by i.r. and mass spectroscopic techniques. The i.r. spectrum of the final product, believed to be perfluoro-(3-methyl-2-oxa-3-azabicyclo[2,2,1]heptane), showed bands at 7.02, 7.29, 7.35, 7.55, 7.84, 8.11, 8.33, 8.78, 9.08, 9.64, 10.18, 10.4, 11.60, and 13.71  $\mu$ , while its mass spectrum showed a molecular ion at m/e 311 and the expected fragmentation pattern.

Reactions of Perfluorocyclopentene. (a) With ethylene. Equimolar mixtures of perfluorocyclopentene and ethylene, contained in 300-ml. Dreadnought ampoules, were heated at  $110^{\circ}/3$  days,  $190^{\circ}/3.75$  days, and  $240^{\circ}/1$  day. No reaction occurred in any case, and the reactants were recovered essentially quantitatively. In a reaction between equimolar amounts of ethylene (0.835 g.) and perfluorocyclopentene (6.32 g.) at  $310^{\circ}$  for 18 hr., the fluoro-olefin was recovered in 97% yield, but only 83% of the ethylene was recovered, together with hydrogen and carbon (0.11 g.).

(b) With acetylene. The reactants were recovered quantitatively after an equimolar mixture of perfluorocyclopentene and acetylene had been heated at 260° for 1 day in a 300-ml. Dreadnought ampoule.

(c) With trifluoronitrosomethane. A mixture of perfluorocyclopentene (0.294 g., 1.39 mmoles) and trifluoronitrosomethane (0.137 g., 1.38 mmoles), left at  $20^{\circ}$  for 14

<sup>35</sup> B. Gething, C. R. Patrick, and J. C. Tatlow, *J. Chem. Soc.*, 1961, 1574.

days in a 300-ml. Dreadnought ampoule, gave trifluoronitrosomethane (0.112 g., 1.13 mmoles, 82% recovery), perfluorocyclopentene (0.294 g., 1.39 mmoles, 100% recovery), and O-nitrosobistrifluoromethylhydroxylamine (0.13 mmole, 18%).

Reaction of Perchlorocyclopentadiene with Trifluoronitrosomethane.--Equimolar amounts of perchlorocyclopentadiene (3.80 g., 13.9 mmoles) and trifluoronitrosomethane (1.38 g., 13.9 mmoles), sealed in a 300-ml. Pyrex ampoule, did not appear to have interacted after storage at 20° overnight; thus the mixture was heated at 100° for 3 days, to give perchlorocyclopentadiene (3.80 g., 13.9 mmoles, 100% recovery), trifluoronitrosomethane (1.27 g. 12.8 mmoles, 92% recovery), and traces of trifluoronitromethane, perfluoro(methylenemethylamine), perfluoroethane, carbon dioxide, silicon tetrafluoride, and O-nitrosobistrifluoromethylhydroxylamine (0.04 g., 0.20 mmole, 3%).

Preparation of 1,1,2,2-tetrafluoro-3-vinylcyclobutane. Tetrafluoroethylene (1.60 g., 16.0 mmoles) and butadiene (1.08 g., 20.0 mmoles), heated at 125° for 6 hr. in a 300-ml. Dreadnought tube, gave unchanged tetrafluoroethylene (0.12 g., 1.20 mmoles, 7.5% recovery) and butadiene (0.15 g., 1.20 mmoles)2.78 mmoles, 14% recovery), and 1,1,2,2-tetrafluoro-3vinylcyclobutane (2.20 g., 14.3 mmoles, 97% based on  $C_2F_4$  consumed) (Found: *M*, 153. Calc. for  $C_6H_6F_4$ :  $\vec{M}$ , 154), b. p. 84—85°/766 mm.,  $n_{\rm D}^{20}$  1·3488 (lit.,<sup>15</sup> b. p. 83—85°,  $n_{\rm D}^{25}$  1·3489),  $\lambda_{\rm max}$ . 6·08  $\mu$  (·CH=CH<sub>2</sub> str.).

Mass Spectral Data (m/e values, with assignments and abundances in parentheses).-Dimethyl 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene-5,6-dicarboxylate (XI) 316 0.8%), 7.3%), 301 (C<sub>10</sub>H<sub>3</sub>F<sub>6</sub>O<sub>4</sub><sup>+</sup>; 297  $(C_{11}H_{6}F_{6}O_{4}^{+};$  $(C_{11}H_6F_5O_4^+;$ 26·9%), 286  $(C_9F_6O_4^+;$ 3.2%),28528.7%), 266 (C<sub>10</sub>H<sub>6</sub>F<sub>4</sub>O<sub>4</sub><sup>+</sup>; 263  $(C_{10}H_{3}F_{6}O_{3}^{+};$ 1.5%),  $(C_{10}H_{3}F_{4}O_{4}^{+};$ 2515.4%), 257 (C<sub>9</sub>H<sub>3</sub>F<sub>6</sub>O<sub>4</sub><sup>+</sup>; 18.5%),235  $(C_9H_3F_4O_4^+)$ **9·6%**),  $\mathbf{236}$  $(C_8F_4O_4^+;$ 10.6%), 223 100·0%),  $(C_8F_5O_2^+;$ **7·3%**), 207  $(C_9H_3F_4O_3^+;$  $(C_8H_3F_4O_2^+; 2.1\%), 205 (C_8F_3O_4^+; 15.0\%), 198 (C_7F_6^+;$ 5.7%), 191 (C<sub>8</sub>F<sub>3</sub>O<sub>2</sub><sup>+</sup>; 1.3%), 179 (C<sub>7</sub>F<sub>5</sub><sup>+</sup>; 6.4%), 174  $(C_5F_6^+; 3.3\%), 167 (C_6F_5^+; 1.0\%), 155 (C_5F_5^+; 0.8\%),$ 148  $(C_6F_4^+; 9.1\%)$ , 143  $(C_4F_5^+; 1.0\%)$ , 137  $(C_4F_3O_2^+;$ 0.6%), 136 (C<sub>5</sub>F<sub>4</sub><sup>+</sup>; 0.7%), 129 (C<sub>6</sub>F<sub>3</sub><sup>+</sup>; 2.5%), 124 (C<sub>4</sub>F<sub>4</sub><sup>+</sup>;  $2\cdot2\%$ ), 117 (C<sub>5</sub>F<sub>3</sub><sup>+</sup>;  $4\cdot1\%$ ), 110 (C<sub>6</sub>F<sub>2</sub><sup>+</sup>;  $0\cdot8\%$ ), 93 (C<sub>3</sub>F<sub>3</sub><sup>+</sup>;  $\begin{array}{l} 2\cdot 7\,\%)\,,\,86\,(C_4F_2^{\,+};\,0\cdot 7\,\%),\,74\,(C_3F_2^{\,+};\,0\cdot 7\,\%),\,69\,(CF_3^{\,+};\,2\cdot 1\,\%),\\ 59\,(C_2H_3O_2^{\,+};\,20\cdot 8\,\%),\,43\,(C_5H_3O^{\,+};\,1\cdot 0\,\%),\,31\,(CF^{\,+};\,CH_3O^{\,+};\,1\cdot 0\,\%),\,31\,(CF^{\,+};\,CH_3O^{\,+};\,CH_3O^{\,+};\,1\cdot 0\,\%),\,31\,(CF^{\,+};\,CH_3O^{\,+};\,CH_3O^{\,+};\,1\cdot 0\,\%),\,31\,(CF^{\,+};\,CH_3O^{\,+}$ 12·3%), 15 (CH<sub>3</sub><sup>+</sup>; 20·6%).

1,2,3,4,7,7-Hexafluorobicyclo[2,2,1]hept-2-ene (XII). 202  $(C_7H_4F_6^+; 17.0\%), 174 (C_5F_6^+; 76.1\%), 152 (C_6H_4F_4^+; 76.1\%))$  $\begin{array}{c} (C_{7}LI_{4}I_{6}, 1) & (I_{6}I_{6}I_{7}I_{6}I_{7}, 1) & (I_{5}I_{6}I_{7}, 10^{-1}I_{0}I_{7}), 152 & (C_{6}I_{4}I_{4}I_{4}, 1) \\ (E_{7}I_{6}I_{8}I_{7}I_{7}), 151 & (C_{6}H_{3}F_{4}^{+}; 31\cdot9\%), 138 & (C_{5}H_{2}F_{4}^{+}; 6\cdot0\%), \\ 137 & (C_{5}HF_{4}^{+}; 8\cdot8\%), 133 & (C_{6}H_{4}F_{3}^{+}; 100\cdot0\%), 132 \\ (C_{6}H_{3}F_{3}^{+}; 19\cdot9\%), 124 & (C_{4}F_{4}^{+}; 45\cdot7\%), 119 & (C_{5}H_{2}F_{2}^{+}; 10\cdot2\%), 113 \\ (C_{1}H_{5}I_{7}, 10/1) & (C_{5}F_{3}^{+}; 3\cdot8\%), 114 & (C_{6}H_{4}F_{2}^{+}; 6\cdot1\%), 113 \\ (C_{1}H_{5}I_{7}, 10/1) & (O_{2}I_{7}H_{5}^{+}I_{7}) & (O_{2}I_{7}H_{5}^{+}I_{7}) \\ \end{array}$  $\begin{array}{c} 10 & 2 \\ (C_6H_3F_2^+; 17\cdot1\%), 102 & (C_5H_4F_2^+; 11\cdot3\%), 101 & (C_6H_3F_2^+; 21\cdot1\%), 95 & (C_6H_4F^+; 7\cdot4\%), 93 & (C_3F_3^+; 8\cdot1\%), 88 & (C_4H_2F_2^+; 4\cdot6\%), 83 & (C_5H_4F^+; 17\cdot7\%), 81 & (C_2F_3^+; 5\cdot7\%), 75 & (C_3H_2F_2^+; 10\cdot6\%), 74 & (C_3F_2^+; 3\cdot1\%), 69 & (CF_3^+; 22\cdot8\%), 63 & (C_2H_2F_2^+; 5\cdot7\%), 64 & (CF_3^+; 22\cdot8\%), 64 & (CF_3^+; 2$  $4\cdot 2\%$ ), 57 (C<sub>3</sub>H<sub>2</sub>F<sup>+</sup>; 10.5%), 51 (CHF<sub>2</sub><sup>+</sup>; 11.3%), 39  $(C_{3}H_{3}^{+}; 3.0\%), 31 (CF^{+}; 7.8\%).$ 

1,2,3,4,7,7-Hexafluorobicyclo[2,2,1]hepta-2,5-diene (XIII). Main peaks: 200 ( $C_7H_2F_6^+$ ; 65.0%), 181 ( $C_7H_2F_5^+$ ; 60.0%), 174 ( $C_5F_6^+$ ; 30.0%), 150 ( $C_6H_2F_4^+$ ; 100.0%), 131 ( $C_3F_5^+$ ; 18.0%), 124 (C<sub>4</sub>F<sub>4</sub><sup>+</sup>; 30.0%), 93 (C<sub>3</sub>F<sub>3</sub><sup>+</sup>; 50.0%), 81 $(C_2F_3^+; 43.0\%), 74 (C_3F_2^+; 25.0\%), 69 (CF_3^+; 50.0\%).$ 

1,2,3,4,7,7-Hexafluoro-5-vinylbicyclo[2,2,1]hept-2-ene  7.4%), 181 (C<sub>2</sub>H<sub>2</sub>F<sub>5</sub><sup>+</sup>; 10.3\%), 177 (C<sub>8</sub>H<sub>5</sub>F<sub>4</sub><sup>+</sup>; 2.2\%), 174 ( $C_5F_6^+$ ; 4.9%), 169 ( $C_6H_2F_5^+$ ; 13.1%), 164 ( $C_7H_4F_4^+$ ; 4.0%), 163 (C<sub>7</sub>H<sub>3</sub>F<sub>4</sub><sup>+</sup>; 7.7%), 159 (C<sub>5</sub>H<sub>4</sub>F<sub>5</sub><sup>+</sup>; 4.9%), 158 ( $C_5H_3F_5^+$ ; 2·2%), 151 ( $C_6H_3F_4^+$ ; 4·9%), 150 ( $C_6H_2F_4^+$ 2.6%), 145 (C<sub>4</sub>H<sub>2</sub>F<sub>5</sub><sup>+</sup>; 3.0%), 137 (C<sub>5</sub>HF<sub>4</sub><sup>+</sup>; 2.2%), 133  $(C_6H_4F_3^+; 5.0\%), 132 (C_6H_3F_3^+; 2.7\%), 127 (C_4H_3F_4^+;$ 3.6%), 124 (C<sub>4</sub>F<sub>4</sub><sup>+</sup>; 4.9%), 119 (C<sub>5</sub>H<sub>2</sub>F<sub>3</sub><sup>+</sup>; 4.4%), 115  $(C_6H_5F_2^+; 2\cdot 4\%)$ , 113  $(C_6H_3F_2^+; 2\cdot 2\%)$ , 101  $(C_5H_3F_2^+;$  $3\cdot2\%$ ), 99 (C<sub>5</sub>HF<sub>2</sub><sup>+</sup>; 2·3\%), 97 (C<sub>6</sub>H<sub>6</sub>F<sup>+</sup>; 1·9\%), 95  $(C_6H_4F^+; 3.0\%), 93 (C_3F_3^+; 3.0\%), 88 (C_4H_2F_2^+; 1.6\%), 81$  $(C_2F_3^+; 2.9\%), 77 (C_3H_2F_2^+; 2.8\%), 75 (C_3HF_2^+; 4.0\%),$  $\begin{array}{c} (c_{2}, c_{3}^{+}, c_{3}^$ 31 (CF<sup>+</sup>; 2.7%), 27 (C<sub>2</sub>H<sub>3</sub><sup>+</sup>; 4.2%).

The 19F N.m.r. Spectrum of Perfluorocyclopentadiene.-



The 56.46 Mc./sec. <sup>19</sup>F n.m.r. spectrum of perfluorocyclopentadiene, measured relative to external CF3·CO2H, consists of three distinct absorption regions of equal relative intensities centred at 61.2, 78.2, and 94.4 p.p.m. The lowfield absorption is assigned to the CF<sub>2</sub> fluorines on the basis of previous chemical shift data.36 By comparison with the spectrum of perfluorocyclopentene, which consists of three regions of absorption at 42.3 (complex, assigned to  $CF_2$ ·CF:), 54.0 (complex, assigned to ·CF<sub>2</sub>·CF<sub>2</sub>·CF<sub>2</sub>·), and 75.8 p.p.m. (complex, assigned to •CF:), the absorption at 78.2 p.p.m. in the spectrum of the diene is assigned to the vinylic fluorines of type  $\cdot CF_2 \cdot CF_3$ , while the 94.4 p.p.m. absorption is attributed to the vinylic fluorines of type  $:CF \cdot CF$ . The multiplet structures of these absorptions is characteristic of an AA'PP'X<sub>2</sub> system, and detailed analysis yields the following spin-spin coupling constants (c./sec.):

$$\frac{|J_{AX}| = 7 \cdot 3 |J_{AA}'|}{|J_{PX}| = 6 \cdot 7 |J_{PP}|} = \begin{cases} 16 \cdot 1 J_{AP} \\ 13 \cdot 7 J_{AP'} \end{cases} = \begin{cases} \pm 16 \cdot 0 \\ \pm 8 \cdot 4 \end{cases}$$

The analysis does not enable distinction to be made between  $J_{AP}$  and  $J_{AP'}$ , but it does indicate that these coupling constants are of opposite sign. The absorption at 61.2 p.p.m. (CF<sub>2</sub> nuclei) is a triplet of triplets with spacings  $J_{AX}$  (= $J_{A'X}$ ),  $J_{PX}$  (= $J_{P'X}$ ). The fine structure of the absorptions at 78.2 and 94.4 p.p.m., due to the two types of vinylic fluorine nuclei, can be derived theoretically from quantum mechanical predictions for an AA'PP' system,37 and the pattern thus obtained is modified by the addition of further first-order splittings, triplets with spacings  $J_{AX}$ in the case of the A fluorine nuclei, and triplets with spacings  $J_{PX}$  in the case of the P fluorine nuclei.

One of us (A. C. H.) is indebted to the S.R.C. for a Research Studentship. Dr K. G. Orrell, now a member of staff of the Chemistry Department of the University of Exeter, was responsible for the measurement and interpretation of the n.m.r. spectra.

[6/1469 Received, November 18th, 1966]

<sup>36</sup> E. G. Brame, Anal. Chem., 1962, 34, 591.
<sup>37</sup> J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 140.