

## Diels–Alder Reactions of Polyfluorocyclohexa-1,3-dienes. Part VI.<sup>1</sup> Reactions of Dodecafluorotricyclo[5,2,2,0<sup>2,6</sup>]undeca-2,5,8-triene with Ethylene and Alkynes. A Synthesis of Polyfluorotricyclo[6,2,2,0<sup>2,7</sup>]dodeca-2,4,6,9-tetraenes and 2,3-Disubstituted Hexafluoronaphthalenes

By W. J. Feast,\* W. K. R. Musgrave, and W. E. Preston, Chemistry Department, The University, South Road, Durham City

Dodecafluorotricyclo[5,2,2,0<sup>2,6</sup>]undeca-2,5,8-triene (1) reacts as a diene in Diels–Alder reactions. Pyrolysis of adducts from the triene (1) and alkynes can be controlled to give polyfluorotricyclo[6,2,2,0<sup>2,7</sup>]dodeca-2,4,6,9-tetraenes or 2,3-disubstituted naphthalenes.

DEHYDROFLUORINATION of the Diels–Alder adduct of 1*H*,2*H*-hexafluorocyclopentene with octafluorocyclohexa-1,3-diene gives dodecafluorotricyclo[5,2,2,0<sup>2,6</sup>]undeca-2,5,8-triene (1);<sup>1</sup> commensurate with reasonable expectation this compound undergoes 1,4-cycloaddition reactions, the dienophile adding across C-3 and C-5. A detailed comparison with other fluorinated dienes has not been undertaken, but qualitatively it appears that the reactivity of compound (1) is of the same order as that of perfluorocyclopentadiene<sup>2</sup> and greater than that of perfluorocyclohexa-1,3-diene.<sup>3</sup> Unlike most other polyfluorocyclopentadienes described,<sup>3–5</sup> compound (1)

shows no tendency to undergo Diels–Alder dimerization, an observation attributable to the steric restrictions imposed by the bulky substituents on the diene unit. Since these substituents are not symmetrically disposed with respect to the plane of the pentadiene ring in structure (1), reaction with a simple symmetric dienophile may give a pair of geometrically isomeric Diels–Alder adducts.

*Diels–Alder Reactions.*—The thermal reactions between compound (1) and ethylene (192°), propyne (115°), and but-2-yne (120°) gave in each case high yields of mixtures of the two possible Diels–Alder adducts. The pairs of isomers were separated by fractional sublimation

<sup>1</sup> Part V, W. J. Feast, W. K. R. Musgrave, and W. E. Preston, *J.C.S. Perkin I*, 1972, 1527.

<sup>2</sup> R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G. Orrell, *J. Chem. Soc. (C)*, 1967, 1608.

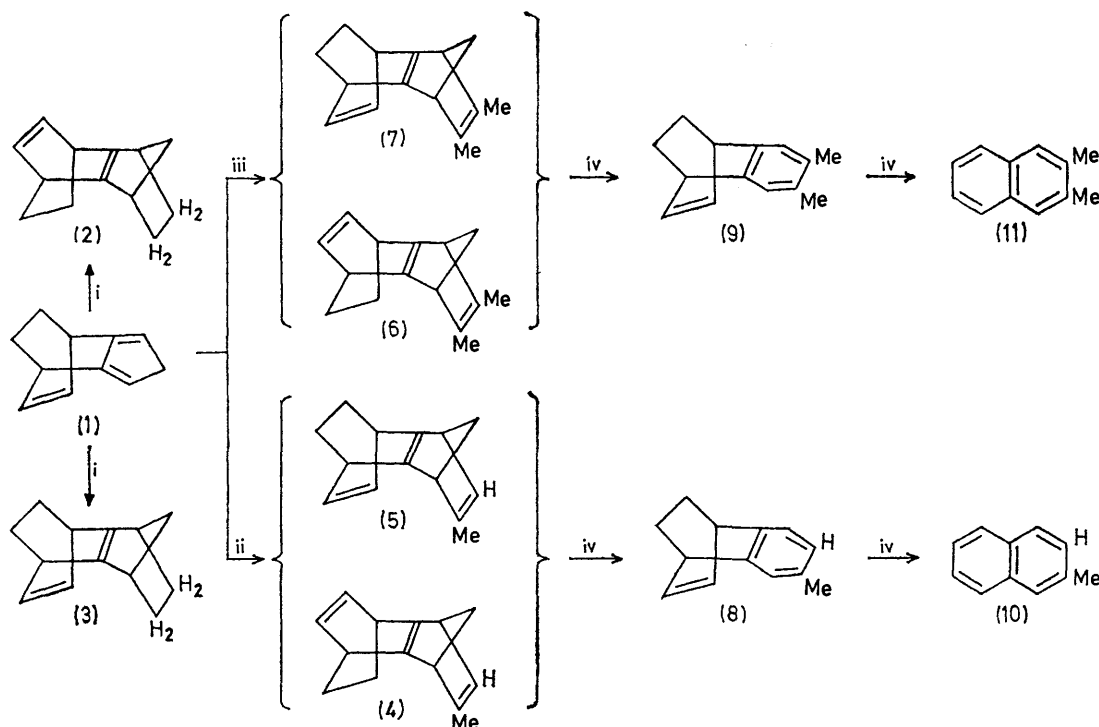
<sup>3</sup> L. P. Anderson, W. J. Feast, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1969, 211.

<sup>4</sup> A. Bergomi, J. Burdon, and J. C. Tatlow, *Tetrahedron*, 1966, 22, 2551.

<sup>5</sup> R. E. Banks, M. Bridge, R. N. Haszeldine, D. W. Roberts, and N. I. Tucker, *J. Chem. Soc. (C)*, 1970, 2531.

followed by recrystallization, the progress of the separation and purification being monitored by analytical g.l.c. All compounds isolated had elemental analyses and mass spectra consistent with their formulation as 1 : 1 adducts, and each displayed a strong i.r. absorption characteristic of a CF=CF double bond. For each pair of isomers the one with the shorter retention time on analytical g.l.c. [*i.e.* (2), (4), or (6)] gave needle-like crystals, whereas the isomer with longer g.l.c. retention time [*i.e.* (3), (5), or (7)] crystallized as platelets. The ratios of the relative abundances of the two isomers were

coupling constants being compatible with those reported for analogous bridging difluoromethylenes in the Diels–Alder adducts of perfluorocyclopentadiene,<sup>3,5</sup> and dimers of highly fluorinated cyclopentadienes.<sup>4,10</sup> Assignment of the detailed stereochemistry is in effect a question of deciding whether the bridging  $-\text{CF}_2\cdot\text{CF}_2-$  of the bicyclic unit  $\alpha$  and the bridging  $-\text{CF}_2-$  of the other bicyclic unit  $\beta$  are on the same or opposite sides of the molecule; if they are on the same side molecular models show that one of the fluorine atoms of the  $-\text{CF}_2-$  will be in close proximity to two of the fluorine atoms of the



SCHEME 1 All unmarked bonds are to fluorine atoms. i,  $\text{CH}_2\cdot\text{CH}_2$ ; ii,  $\text{CH}_3\cdot\text{C}\cdot\text{CH}$ ; iii,  $\text{CH}_3\cdot\text{C}\cdot\text{C}\cdot\text{CH}_3$ ; iv, vacuum pyrolysis

50 : 50, 45 : 55, and 23 : 77 for (2) : (3), (4) : (5), and (6) : (7), respectively. The assignment of structure and detailed stereochemistry of the six adducts is based on their n.m.r. spectra (Table 1). The gross structural features of all the adducts (2)—(7) are established by the chemical shifts and integrated intensities. Thus the bicyclo[2,2,2] unit, labelled  $\alpha$  in the formulae (Table 1), which is present in the initial triene (1) is also present in the adducts and is readily identified by the characteristic tertiary, vinylic and bridging  $-\text{CF}_2\cdot\text{CF}_2-$  resonances in the  $^{19}\text{F}$  n.m.r. spectra.<sup>1,2,6-9</sup> The resonances remaining are the characteristic high-field signals due to the two tertiary fluorine atoms in the bicyclo[2,2,1] unit, labelled  $\beta$  in the formulae (Table 1), and an AB quartet for the bridging difluoromethylene, the range of observed

$-\text{CF}_2\cdot\text{CF}_2-$  bridge and we should expect some evidence of spin–spin interaction. A comparison of the  $-\text{CF}_2-$  and  $-\text{CF}_2\cdot\text{CF}_2-$  resonances of the pairs of isomers (4) and (5), and (6) and (7) provides evidence for such an interaction. In the spectra of compounds (5) and (7) the components of one limb of the AB quartet due to the  $-\text{CF}_2-$  are split into a seven-line multiplet and the signal due to the bridging  $-\text{CF}_2\cdot\text{CF}_2-$  is broad and asymmetric, whereas for the compounds (4) and (6) the components of both limbs of the  $-\text{CF}_2-$  AB quartet are sharp single lines and the bridging  $-\text{CF}_2\cdot\text{CF}_2-$  gives a narrower symmetrical signal. Consistent with the structural assignment based on these observations is separation of the vinylic fluorine signals in the spectrum of compound (5) resulting from their relatively close proximity to the asymmetrically substituted double bond; in the case of

<sup>6</sup> L. P. Anderson, W. J. Feast, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1969, 2559.

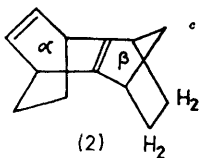
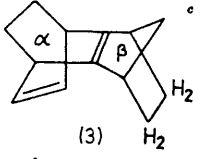
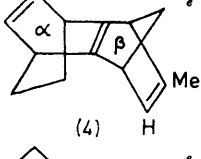
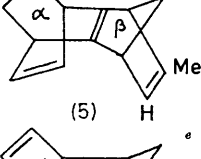
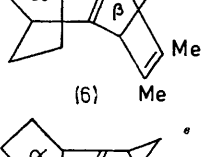
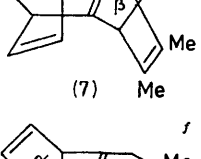
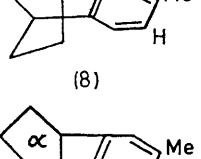
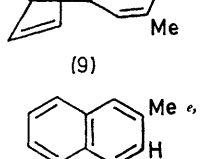
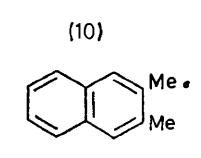
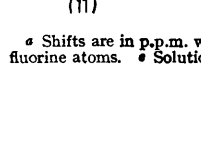
<sup>7</sup> W. J. Feast, W. K. R. Musgrave, and R. G. Weston, *J. Chem. Soc. (C)*, 1971, 937, 1547.

<sup>8</sup> R. E. Banks, L. E. Birks, M. Bridge, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1970, 2539.

<sup>9</sup> A. B. Clayton, W. J. Feast, D. R. Sayers, R. Stephens, and J. C. Tatlow, *J. Chem. Soc. (C)*, 1971, 1183.

<sup>10</sup> R. Fields, M. Green, and A. Jones, *J. Chem. Soc. (B)*, 1967, 270.

TABLE I  
 N.m.r. spectral parameters <sup>a</sup>

Compound <sup>b</sup>	$\alpha$			$\beta$		Aromatic F	CH <sub>3</sub> -	H-	-CH <sub>2</sub> -CH <sub>2</sub> -		
	-C-F	=C-F	-CF <sub>2</sub> -CF <sub>2</sub> -	-C-F	-CF <sub>2</sub> -						
 (2) H <sub>2</sub>	216.9(2)	153.1(2)	$\delta_A$ 123.9(2) <sup>d</sup> $\delta_B$ 118.8(2) $J_{AB}$ 215	198.4(2)	$\delta_A$ 152.2(1) $\delta_B$ 140.6(1) $J_{AB}$ 171				2.58(2) 2.02(2)		
 (3) H <sub>2</sub>	217.2(2)	153.2(2)	$\delta_A$ 124.8(2) <sup>d</sup> $\delta_B$ 118.5(2) $J_{AB}$ 215	200.0(2)	$\delta_A$ 153.1(1) $\delta_B$ 128.8(1) $J_{AB}$ 171				2.47		
 (4) H	216.9(2)	153.4(2)	122.0(4)	205.2(1) 199.9(1)	$\delta_A$ 137.3(1) $\delta_B$ 133.6(1) $J_{AB}$ 146		1.97(3)	6.33(1)			
 (5) H	217.6(2)	153.5(1) 152.1(1)	120.6(4)	205.0(1) 199.9(1)	$\delta_A$ 132.1(1) $\delta_B$ 125.7(1) $J_{AB}$ 140		2.02(3)	6.42(1)			
 (6) Me	216.7(2)	153.1(2)	122.3(4)	205.7(2)	$\delta_A$ 136.3(1) $\delta_B$ 133.1(1) $J_{AB}$ 152		1.87				
 (7) Me	217.3(2)	153.0(2)	120.7(4)	206.4(2)	$\delta_A$ 134.1(1) $\delta_B$ 126.2(1) $J_{AB}$ 144		1.85				
 (8) Me	216.4(2)	153.9(2)	$\delta_A$ 125.8(2) <sup>d</sup> $\delta_B$ 123.4(2) $J_{AB}$ 221			125.6(1)	128.6(1)	2.38(3)	7.08(1)		
 (9) Me	216.7(2)	153.9(2)	124.8(4)				127.8(2)	2.30			
 (10) Me						122.5(1)	126.5(1)	145.6(1) 146.8(1)	155.5(1) 157.7(1)	2.43(3)	7.00(1)
 (11) Me						125.8(2)	147.1(2)	158.6(2)	2.30		

<sup>a</sup> Shifts are in p.p.m. with respect to internal CCl<sub>3</sub> or Me<sub>4</sub>Si as reference; integrated intensities in parentheses; coupling constants in Hz. <sup>b</sup> Unmarked valencies to fluorine atoms. <sup>c</sup> Solution in acetone for <sup>19</sup>F, [<sup>2</sup>H<sub>4</sub>] acetone for <sup>1</sup>H. <sup>d</sup> Pseudo AB quartet. <sup>e</sup> Solution in CCl<sub>4</sub>. <sup>f</sup> Neat liquid. <sup>g</sup> External Me<sub>4</sub>Si.

the geometrical isomer (4) where the vinylic fluorines are well separated from the influence of the  $\text{CH}_3\text{-C=C-H}$  unit, they appear as a single resonance. The stereochemistry of isomers (2) and (3) was deduced from a comparison of the crystalline form, relative g.l.c. retention time, and n.m.r. spectral parameters of this pair and the pairs (4) and (5), and (6) and (7).

**Pyrolyses.**—Elimination of either the difluoromethylene group or the  $-\text{CF}_2\cdot\text{CF}_2-$  bridge from adducts (4)—(7) leads to the formation of an aromatic ring, and may be accomplished in a stepwise manner. The difluoromethylene group is much more readily eliminated than  $-\text{CF}_2\cdot\text{CF}_2-$ ; thus, compound (7) gives (9) in 65% yield on pyrolysis in a flow system at  $380^\circ$  and  $10^{-3}$  mmHg, and a mixture of compounds (4) and (5) gives (8) in 37% yield when heated in a sealed tube at  $200^\circ$ . Pyrolysis at or above  $600^\circ$  at  $10^{-3}$  mmHg in a flow system results in the elimination of all bridges, thus compounds (4), (5), and (8) give (10), whereas (9) gives (11) under these conditions. The products of these pyrolysis reactions, *i.e.* the decafluorotricyclo[6,2,2,0<sup>2,7</sup>]dodeca-2,4,6,9-tetraenes (8) and (9) and the 2,3-disubstituted hexafluoronaphthalenes (10) and (11), are of kinds not previously available and it is to be expected that analogous structures with different substituents may be synthesised by the same route. The structures of compounds (8)—(11) follow from their mode of preparation, elemental analyses, and mass spectra: their i.r., u.v., and n.m.r. spectra confirm the assigned structures. Thus, for both compounds (8) and (9) the i.r. spectrum indicates the presence of a  $\text{CF}=\text{CF}$  double bond, and the  $^{19}\text{F}$  n.m.r. data confirm the expected bicyclo[2,2,2] unit (labelled  $\alpha$ ; see Table 1), together with two aromatic fluorine atoms. In the mass spectra of both compounds (8) and (9) the base peak corresponds to the loss of 100 mass units ( $\text{C}_2\text{F}_4$ ) from the molecular ion, whereas for both (10) and (11) the base peak is the molecular ion. The  $^{19}\text{F}$  n.m.r. spectra of the hexafluoronaphthalenes (10) and (11) are not first-order and the coupling constants have not been elucidated; however it is clear that the expected large (*ca.* 60 Hz) *peri* F—F coupling<sup>11</sup> is present in both compounds and that the *peri*-fluorine atoms are those resonating at 145.6 and 146.8 p.p.m. for the aromatic ring carrying four fluorines in (10) and at 122.5 and 126.5 for the other ring, the analogous *peri*-fluorine signals in (11) being at 147.1 and 125.8, respectively. As expected,<sup>12</sup> u.v. spectra of compounds (10) and (11) resembled those of naphthalene and octafluoronaphthalene (Table 2), the bathochromic shift of the bands in (10) and (11) being qualitatively consistent with their substitution pattern.<sup>13</sup>

The pyrolysis of adducts (4) and (5) may be carried out either in a sealed vessel or under reduced pressure in a flow system; in the latter method a clean reaction is observed and only the products of elimination of the  $>\text{CF}_2$  and  $-\text{CF}_2\cdot\text{CF}_2-$  bridges are formed, but in pyrolyses

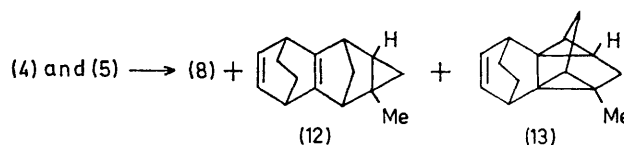
in sealed vessels the eliminated group remains in the hot reaction zone and may react with the original starting material or its primary pyrolysis products and consequently a more complex reaction product may result.

TABLE 2  
U.v. spectra<sup>a</sup>

Compound	$\lambda_{\text{max.}}/\text{nm}$ ( $\log_{10} \epsilon$ )		
Naphthalene	275 (3.75)	312 (2.4)	
Octafluoronaphthalene	277 (3.67)	308 (3.22)	322.5 (3.31)
(10)	283 (3.64)	316 (3.54)	330 (3.69)
(11)	285 (3.50)	315 (3.40)	329 (3.53)

<sup>a</sup> In cyclohexane, recorded on Unicam SP 800 spectrophotometer.

In the reaction of propyne with the triene (1) in a sealed tube at  $200^\circ$  the product consisted of at least four components. The major product was (8) (37% yield) and results from expulsion of difluoromethylene from the intermediate Diels–Alder adducts (4) and (5). Two other products were isolated from the mixture and identified as (12) (7.3% yield), resulting from addition of difluoromethylene to (4) and/or (5); and (13) (2.3% yield), an isomerization product of (12); none of compounds (4) and (5) was recovered when the reaction was run at this temperature. The assignment of structures (12) and



SCHEME 2 All unmarked bonds are to fluorine atoms

(13) is based on their mode of formation, elemental analysis, and spectra. The compound (12) had a highest mass peak in its mass spectrum at  $m/e$  450, which corresponds to the molecular ion of a product arising from (4) or (5) +  $\text{CF}_2$  or (8) +  $\text{C}_2\text{F}_4$ . The latter possibility was excluded by heating compound (8) in a sealed tube with tetrafluoroethylene: no trace of (12) or (13) was observed; thus compound (12) probably arises from addition of difluoromethylene to (4) or (5) and the most likely site of attack for this electrophilic reagent would be the methyl-substituted double bond. Conclusive proof of this mode of formation was obtained from heating a mixture of the two Diels–Alder adducts (4) and (5) in a sealed tube under the reaction conditions already mentioned. Analysis of the product mixture by g.l.c. and i.r. spectroscopy showed the absence of (4) and (5) and the presence of (8) as the major component of the mixture; minor products had the same retention times as compounds (12) and (13). The presence of the bicyclo[2,2,2]octadiene unit in (12) is supported by the observation of the characteristic  $-\text{CF}=\text{CF}-$  double bond stretching frequency at  $1754\text{ cm}^{-1}$  in the i.r. spectrum, the typical tertiary, vinylic, and bridging  $-\text{CF}_2\cdot\text{CF}_2-$  resonances in the  $^{19}\text{F}$  n.m.r. spectrum, and the formation of the base peak in the mass spectrum by expulsion

<sup>11</sup> R. A. Fletton, R. D. Lapper, and L. F. Thomas, *Chem. Comm.*, 1969, 1049.

<sup>12</sup> D. Harrison, M. Stacey, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 1963, 19, 1893.

<sup>13</sup> J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963.

of 100 mass units ( $C_2F_4$ ) from the molecular ion. Signals for two other tertiary fluorine atoms are present in the  $^{19}F$  n.m.r. spectrum, together with a difluoromethylene signal which overlaps with the bridging  $-CF_2\cdot CF_2-$  resonances, and an AB quartet which corresponds both in shift and magnitude of coupling constant (178 Hz) with a cyclopropyl difluoromethylene group.<sup>14</sup> The structure of compound (13) was also established on the basis of elemental analysis and spectroscopic examination. Compound (13) is isomeric with (12) and its spectra are qualitatively similar, suggesting a structural similarity; the two major differences between the spectra of (12) and (13) are that the base peak in the mass spectrum of (13) does not arise by expulsion of 100 mass units from the molecular ion and that the low field AB quartet in the  $^{19}F$  n.m.r. spectrum of (13) has a coupling constant of 250 Hz as opposed to 178 Hz for (12). The expulsion of 100 mass units ( $C_2F_4$ ) is a prominent feature of the mass spectra of all the compounds containing the bicyclo[2,2,2]octadiene unit which we have examined,<sup>1,2,6,7</sup> and its occurrence may be rationalized on the basis that elimination of the  $-CF_2\cdot CF_2-$  bridge from these compounds produces an aromatic unit; the reduced importance of this expulsion of  $C_2F_4$  in the spectrum of (13) is therefore consistent with the structure assigned (Scheme 2). Further, the magnitude of the coupling constant of the low-field AB quartet in the  $^{19}F$  n.m.r. spectrum is compatible with a difluoromethylene group in either of the environments present in (13), but excludes a three-membered ring.<sup>14</sup> This isomerization (12)  $\rightarrow$  (13) is analogous to that [(14)  $\rightarrow$  (15)]



reported by Sargeant, and probably proceeds *via* a carbonium-ion mechanism<sup>14</sup> rather than a non-concerted [ $\pi_2 + \sigma_2$ ] transannular cycloaddition.<sup>15</sup>

#### EXPERIMENTAL

**General.**—Techniques and apparatus were as described previously.<sup>7</sup> Perfluorotricyclo[5,2,2,0<sup>2,6</sup>]undeca-2,5,8-triene was prepared by the previously described route.<sup>1</sup> N.m.r. references were internal  $CFCl_3$  and  $Me_4Si$  unless otherwise stated.

**Diels-Alder Reactions of Perfluorotricyclo[5,2,2,0<sup>2,6</sup>]undeca-2,5,8-triene (1).**—(a) *With ethylene.* A mixture of the triene (1) (1.66 g, 4.62 mmol) and ethylene (4.78 mmol) was sealed *in vacuo* in a Pyrex ampoule (130 ml), which was heated at 192° for 16.5 h to give: (i) ethylene (1.67 mmol); (ii) a colourless liquid (0.36 g), shown by i.r. spectroscopy and analytical g.l.c. to be predominantly the triene (1); (iii) a white solid (1.22 g), shown by analytical g.l.c. to consist of two components in approximately equal proportions. This mixture was separated into its components by fractional sublimation (20° at  $10^{-3}$  mmHg) to give the two isomers of 4H,4H,5H,5H-dodecafluorotetracyclo-

[6,2,2,1<sup>3,6,7</sup>]trideca-2(7),9-diene (2) and (3). For the isomer (2) with the shorter g.l.c. retention time: [Found: C, 40.0; H, 1.15; F, 59.0%;  $M$  (mass spectrometry), 388.  $C_{13}H_4F_{12}$  requires C, 40.2; H, 1.0; F, 58.7%;  $M$ , 388], fine needles, m.p. 77–77.5° (from acetone),  $\nu_{max}$  1754 ( $-CF=CF-$ ) and 1623  $cm^{-1}$  ( $>C=C<$ ). For the isomer (3) with the longer g.l.c. retention time: [Found: C, 40.0; H, 1.2; F, 59.1%;  $M$  (mass spectrometry), 388], platelets, m.p. 126.5–127° (from acetone),  $\nu_{max}$  1754 ( $-CF=CF-$ ) and 1630  $cm^{-1}$  ( $>C=C<$ ).

(b) *With propyne.* Experiment 1. By the same procedure as in (a), triene (1) (2.56 g, 7.10 mmol) and propyne (7.43 mmol) were heated in a Pyrex ampoule (120 ml) at 115° for 65 h to give (i) propyne (2.2 mmol) (i.r. spectrum); (ii) a colourless liquid (0.88 g) shown by i.r. spectroscopy and g.l.c. to be the triene (1) containing <10% of (4) and (5); (iii) a white solid (1.88 g) shown by analytical g.l.c. to contain two components in the ratio 45:55. This mixture was separated by fractional sublimation ( $10^{-3}$  mmHg, 60°) followed by fractional crystallization to give the two isomers of 4H-dodecafluoro-5-methyltetracyclo[6,2,2,1<sup>3,6,7</sup>]trideca-2(7),4,9-triene (4) and (5). For the isomer (4) with the shorter g.l.c. retention time: [Found: F, 56.5%;  $M$  (mass spectrometry), 400.  $C_{14}H_4F_{12}$  requires F, 57.0%;  $M$ , 400], fine needles, m.p. 81–82° [from petroleum (b.p. 60–80°)],  $\nu_{max}$  1755 ( $-CF=CF-$ ), 1640 and 1605  $cm^{-1}$  ( $-CH=CMe-$  and  $>C=C<$ ). For the isomer (5) with the longer g.l.c. retention time: [Found: F, 56.9%;  $M$  (mass spectrometry), 400], platelets, m.p. 63–64° [from petroleum (b.p. 60–80°)],  $\nu_{max}$  1755 ( $-CF=CF-$ ), 1640 and 1612  $cm^{-1}$  ( $-CH=CMe-$  and  $>C=C<$ ).

Experiment 2. By the same procedure as in (a), the triene (1) (2.0 g, 5.81 mmol) and propyne (6.14 mmol) were heated in a Pyrex ampoule (120 ml) at 200° for 52 h to give a gaseous mixture (1.47 mmol), shown by i.r. spectroscopy to contain propyne, silicon tetrafluoride, and tetrafluoroethylene; and a liquid mixture (2.0 g). The liquid mixture was shown to contain several components by analytical g.l.c., of which the four major components were obtained pure by preparative g.l.c. [Silicone Elastomer on Celite (1:2), 150°,  $N_2$  carrier]; in order of emergence from the column they were (i) triene (1) (0.08 g, 0.22 mmol) (i.r. spectrum); (ii) 4H-tetradecafluoro-6-methylhexacyclo[7,2,2,1<sup>3,7,0,2,4,0,2,8,0,6,8</sup>]tetradec-10-ene (13) (0.06 g, 0.133 mmol, 2.3%) [Found: F, 59.6%;  $M$  (mass spectrometry), 450.  $C_{15}H_4F_{14}$  requires F, 59.1%;  $M$ , 450], a colourless solid,  $\nu_{max}$  1757  $cm^{-1}$  ( $-CF=CF-$ );  $^{19}F$  n.m.r. spectrum 230.3 (1F), 222.8 (1F), 212.6 (1F), and 213.4 (1F) (fluorines at tertiary sites), 150.2 (1F) and 151.0 (1F) (vinylic fluorines), 127.3 (4F, bridging  $CF_2\cdot CF_2$ ), 121.2 p.p.m. (2F,  $CF_2$ ), and an AB quartet (2F,  $\delta_A$  100.1,  $\delta_B$  118.2,  $J_{AB}$  250 Hz,  $CF_2$ );  $^1H$  n.m.r. spectrum  $\delta$  1.27 (3H) and 2.73 p.p.m. (1H, d,  $J$  15 Hz);  $m/e$  450 (19.0%), 431 (6.9), 381 (10.3), 350 (37.9), 335 (6.9), 331 (10.3), 300 (12.1), 285 (12.1), 281 (69.0), 250 (56.9), 249 (16.6), 231 (22.4), 219 (20.7), 127 (100), 113 (8.6), 100 (5.2), and 69 (10.3); (iii) 4H-tetradecafluoro-6-methylpentacyclo[7,2,2,1<sup>3,7,0,4,6,0,2,8</sup>]tetradeca-2(8),10-diene (12) (0.19 g, 0.422 mmol, 7.3%) [Found: F, 58.5%;  $M$  (mass spectrometry) 450], a colourless solid,  $\nu_{max}$  1754  $cm^{-1}$  ( $-CF=CF-$ );  $^{19}F$  n.m.r. spectrum 238.4 (1F), 219.6 (1F), and 212.7 (2F) (fluorines at tertiary sites), 151.7 (1F) and 150.6

<sup>14</sup> P. B. Sargeant, *J. Amer. Chem. Soc.*, 1969, **91**, 3061.

<sup>15</sup> R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie GmbH/Academic Press Inc., 1970, reprinted from *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

(1F) (vinylic fluorines), a series of eight bands between 135.2 and 121.7 p.p.m. (6F, bridging  $\text{CF}_2\text{-CF}_2$  and the  $\text{CF}_2$  bridge between C-3 and C-7), and an AB quartet (2F,  $\delta_A$  106.2,  $\delta_B$  125.7,  $J_{AB}$  178 Hz,  $\text{CF}_2$  of the three-membered ring);  $^1\text{H}$  n.m.r. spectrum  $\delta$  1.55 (3H,  $\text{CH}_3$ ) and 3.12 p.p.m. (1H, tertiary);  $m/e$  450 (11.9%), 381 (13.1), 350 (100), 335 (52.4), 331 (19.1), 300 (14.3), 299 (14.3), 285 (33.3), 281 (81.0), 250 (45.2), 249 (21.4), 231 (33.3), 113 (31.0), 109 (19.1), 100 (15.5), and 69 (21.4); (iv) 4H-decafluoro-5-methyltricyclo[6,2,2,0<sup>2,7</sup>]dodeca-2,4,6,9-tetraene (8) (0.75 g, 2.14 mmol, 36.8%) [Found: C, 44.8; H, 1.2; F, 53.8%;  $M$  (mass spectrometry), 350.  $\text{C}_{13}\text{H}_4\text{F}_{10}$  requires C, 44.6; H, 1.2; F, 54.3%;  $M$ , 350], a colourless liquid,  $\nu_{\text{max}}$  1773 ( $-\text{CF}=\text{CF}-$ ),  $\lambda_{\text{max}}$  272 ( $\epsilon$  1800) and 279 nm (2160).

(c) *With but-2-yne*. By the same procedure as in (a) the triene (1) (4.60 g, 12.8 mmol) and but-2-yne (0.77 g, 14.3 mol) were heated in a Pyrex ampoule (100 ml) at 120° for 64.5 h to give: (i) a volatile fraction (0.88 g) shown by i.r. spectroscopy to be a mixture of triene (1) and but-2-yne; (ii) a white solid (4.38 g) shown by analytical g.l.c. to contain two components in the ratio 23 : 77. This mixture was separated by fractional sublimation ( $10^{-3}$  mmHg, 80°) followed by fractional crystallization to give the two isomers of dodecafluoro-4,5-dimethyltetracyclo[6,2,2,1<sup>3,6</sup>,0<sup>2,7</sup>]trideca-2(7),4,9-triene, (6) and (7). For the isomer (6) with the shorter g.l.c. retention time, the minor component: [Found: C, 43.9; H, 1.2; F, 55.2%;  $M$  (mass spectrometry), 414.  $\text{C}_{15}\text{H}_6\text{F}_{12}$  requires C, 43.5; H, 1.5; F, 55.0%;  $M$ , 414], fine needles, m.p. 64.5–65° (from methanol),  $\nu_{\text{max}}$  1760 ( $-\text{CF}=\text{CF}-$ ) and 1620  $\text{cm}^{-1}$  ( $-\text{CMe}=\text{CMe}-$  or  $>\text{C}=\text{C}<$ ). For the isomer (7) with the longer g.l.c. retention time, the major component: [Found: C, 43.2; H, 1.2; F, 54.6%;  $M$  (mass spectrometry), 414], platelets, m.p. 82–82.5° [from petroleum (b.p. 60–80°)],  $\nu_{\text{max}}$  1760 ( $-\text{CF}=\text{CF}-$ ) and 1630  $\text{cm}^{-1}$  ( $-\text{CMe}=\text{CMe}-$  or  $>\text{C}=\text{C}<$ ).

*Vacuum Pyrolyses*.—The apparatus used and procedure adopted were as previously described.<sup>7</sup>

(a) Compound (8) (0.27 g, 0.77 mmol) was pyrolysed at 540° and  $10^{-3}$  mmHg then at 630° and  $10^{-3}$  mmHg to give: (i) a gas mixture (0.78 mmol), shown by mass and i.r. spectroscopy to be predominantly tetrafluoroethylene with a trace of silicon tetrafluoride; (ii) a yellow solid, sublimed (70° and  $10^{-3}$  mmHg) to give a colourless solid, 2H-hexafluoro-3-methylnaphthalene (10) (0.134 g, 0.54 mmol, 70%) [Found: C, 53.0; H, 1.9; F, 45.1%;  $M$  (mass spectrometry), 250.  $\text{C}_{11}\text{H}_4\text{F}_6$  requires C, 52.8; H, 1.6; F, 45.6%;  $M$ , 250], m.p. ca. room temperature.

(b) An equimolar mixture of compounds (4) and (5)

(0.207 g, 0.52 mmol) was pyrolysed at 640° and  $10^{-3}$  mmHg to give (i) a gas mixture (0.84 mmol), shown by mass and i.r. spectroscopy to be predominantly tetrafluoroethylene with a trace of silicon tetrafluoride; (ii) a yellow solid which gave as a colourless solid after sublimation (70° and  $10^{-3}$  mmHg) 2H-hexafluoro-3-methylnaphthalene (10) (0.072 g, 0.288 mmol, 55.4%) (i.r. spectrum).

(c) Compound (7) (0.813 g, 1.96 mmol) was pyrolysed at 380° and  $10^{-3}$  mmHg to give (i) tetrafluoroethylene (0.995 mmol), identified by i.r. and mass spectroscopy; (ii) dodecafluoro-4,5-dimethyltricyclo[6,2,2,0<sup>2,7</sup>]dodeca-2,4,6,9-tetraene (9) (0.462 g, 1.27 mmol, 64.8%) [Found: C, 46.4; H, 2.0; F, 51.9%;  $M$  (mass spectroscopy), 364.  $\text{C}_{14}\text{H}_6\text{F}_{10}$  requires C, 46.2; H, 1.7; F, 52.2%;  $M$ , 364], m.p. 66–67° [from petroleum (b.p. 60–80°)],  $\nu_{\text{max}}$  1779  $\text{cm}^{-1}$  ( $-\text{CF}=\text{CF}-$ ),  $\lambda_{\text{max}}$  272 ( $\epsilon$  2680) and 279 nm (2850).

(d) Compound (9) (0.245 g, 0.673 mmol) was pyrolysed at 600° and  $10^{-3}$  mmHg to give (i) a gas mixture (0.363 mmol) shown by mass and i.r. spectroscopy to be predominantly tetrafluoroethylene with a trace of silicon tetrafluoride; (ii) a yellow solid (0.198 g), recrystallised from petroleum (b.p. 60–80°) to give as a colourless solid in quantitative yield, 2,3-dimethylhexafluoronaphthalene (11), m.p. 120–121° [Found: C, 54.3; H, 2.5%;  $M$  (mass spectrometry), 264.  $\text{C}_{12}\text{H}_6\text{F}_6$  requires C, 54.6; H, 2.3%;  $M$ , 264].

*Treatment of the Tricyclicododecatetraene (8) with Tetrafluoroethylene*.—A mixture of compound (8) (0.057 g, 0.163 mmol) and tetrafluoroethylene (0.082 mmol) was sealed under vacuum in a Pyrex ampoule (5 ml) and heated at 200° for 68 h to give (i) tetrafluoroethylene (i.r. spectrum) and (ii) compound (8) (0.032 g) (i.r. spectrum).

*Heating the Tetracyclicododecatetraenes (4) and (5)*.—An equimolar mixture of compounds (4) and (5) (0.10 g, 0.25 mmol) was sealed under vacuum in a Pyrex ampoule (70 ml), which was heated at 200° for 90 h to give (i) a gas (0.077 mmol) (discarded), and (ii) a colourless liquid (0.076 g). Analytical g.l.c. of this mixture and of the mixture enriched with authentic samples of compounds (8), (12), and (13) established that the mixture contained four components. The major component had a retention time identical with that of compound (8) and the two minor components had retention times identical with those of compounds (12) and (13). The fourth component was present in trace amounts only. The i.r. spectrum of the mixture was entirely consistent with its being predominantly compound (8) with small concentrations of (12) and (13).

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