

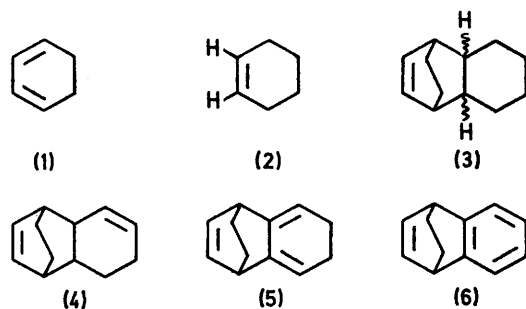
Diels–Alder Reactions of Polyfluorocyclohexa-1,3-dienes. Part 7.¹ Reactions of Perfluorotricyclo[6.2.2.0^{2,7}]dodeca-2,6,9-triene

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The synthesis of perfluorotricyclo[6.2.2.0^{2,7}]dodeca-2,6,9-triene (5) *via* dehydrofluorination of the Diels–Alder adduct (3) of perfluorocyclohexa-1,3-diene and 1*H*,2*H*-octafluorocyclohexene has been reinvestigated, and the overall yield improved. Dehydrofluorination of the adduct (3) in a flow system over sodium fluoride pellets is complicated by the 1,2-elimination of fluorine from the triene (5) to give perfluoro-1,4-dihydro-1,4-ethanonaphthalene (6). The diene moiety of the triene (5) is reactive in Diels–Alder additions with alkenes and alkynes. The stereoselectivity of such additions is not consistent with the existence of a strong secondary orbital interaction with the neighbouring non-conjugated double bond.

We have previously reported the Diels–Alder reaction of octafluorocyclohexa-1,3-diene (1) with 1*H*,2*H*-octafluorocyclohexene (2), and the dehydrofluorination of the adduct (3) to give perfluorotricyclo[6.2.2.0^{2,7}]dodeca-2,6,9-triene (5).² Neither of the steps in this synthesis proceeded in good yield, and we therefore re-examined the synthesis as a preliminary to a study of the chemistry of the triene (5).

In the temperature range required to obtain reaction between the diene (1) and the olefin (2) the diene also



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undergoes Diels–Alder dimerization^{2,3} to give the tricyclo-diene (4) and isomerization to perfluorocyclohexa-1,4-diene.^{4,5} However under optimal conditions (see Experimental section) the yield for the first step was increased from the 17% reported previously to >30%, with a good material balance (>95%) allowing the

¹ Part 6, W. J. Feast, W. K. R. Musgrave, and W. E. Preston, *J.C.S. Perkin I*, 1972, 1830.

² W. J. Feast, W. K. R. Musgrave, and W. E. Preston, *J.C.S. Perkin I*, 1972, 1527.

³ L. P. Anderson, W. J. Feast, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1969, 2559; L. P. Anderson, Ph.D. Thesis, Durham University, 1969.

⁴ B. Gething, C. R. Patrick, J. C. Tatlow, R. E. Banks, A. K. Barbour, and A. E. Tipping, *Nature*, 1959, 183, 586.

greater part of the unchanged starting materials to be recycled so that the process gave acceptable overall conversions into (3).

Dehydrofluorination of the adduct (3) was previously accomplished by refluxing with aqueous potassium hydroxide.² A series of experiments has now been carried out in an attempt to define optimal conditions for this step, and although some measure of control was obtained (see Experimental section) the process retained an element of unpredictability. Several other techniques of dehydrofluorination which had proved successful with other systems were attempted (use of molten potassium hydroxide,⁶ powdered potassium hydroxide in benzene,⁷ or an anion-exchange resin⁸) but none provided a satisfactory alternative route from (3) to (5); however, dehydrofluorination of (3) in the vapour phase over sodium fluoride⁹ pellets did occur. With heated nitrogen as carrier gas, the adduct (3) was passed in the vapour phase over sodium fluoride pellets maintained at 365 °C. At this temperature conversions into the triene (5) were about the same as those obtained by the aqueous potassium hydroxide techniques, *i.e.* 20–30%. Unfortunately the required triene (5), was accompanied by perfluoro-1,4-dihydro-1,4-ethanonaphthalene (6), together with traces of perfluoro-1,2-dihydronaphthalene and perfluoronaphthalene. Increasing the temperature of reaction or the contact time increased the proportions of compound (6), perfluoro-1,2-dihydro-

⁵ A. M. Doyle, C. R. Patrick, and A. E. Pedler, *J. Electroanal. Chem.*, 1971, 33, 23.

⁶ J. Burdon, T. M. Hodgins, D. R. A. Perry, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 808.

⁷ D. J. Dodsworth, C. M. Jenkins, R. Stephens, and J. C. Tatlow, *J.C.S. Chem. Comm.*, 1972, 803.

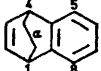
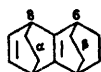
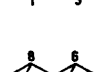
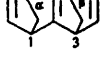
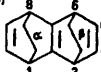
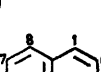
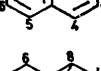
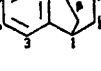
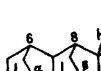
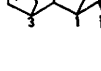
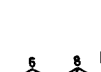
⁸ R. E. Banks, W. I. Bevan, and W. K. R. Musgrave, *Chem. and Ind.*, 1959, 296.

⁹ R. Stephens, J. C. Tatlow, and M. Stacey, *Fr. Pat.* 1 351 152 (*Chem. Abs.*, 1964, 60, 11917h); R. Stephens and J. C. Tatlow, *Belg. Pat.* 625 313 (*Chem. Abs.*, 1963, 59, 9836c).

naphthalene, and naphthalene in the product, whereas lower temperatures resulted in lower conversions of (3) into (5). Since the presence of the secondary products described above considerably complicated the recovery and purification of the triene (5) this dehydrofluorination technique offers no practical advantages over the method

spectrum was indicative of an aromatic system and qualitatively similar to those of polyfluoro-1,4-dihydro-1,4-ethanonaphthalenes reported previously;¹ and the ¹⁹F n.m.r. spectrum (Table I) showed resonances in the typical regions for tertiary (>C-F), vinylic (:C-F) and bridging (>CF₂) groups, along with two different

TABLE I
N.m.r. spectral parameters^a

Compound ^b	α			β		Cyclopentane CF ₂	Aromatic F	¹ H	
	>C-F	=C-F	-CF ₂ CF ₂ -	>C-F	-CF ₂ CF ₂ -				
(6)		218.2(2) <i>J</i> _{1,3(4,5)} 36	158.0(2)	δ _A 124.2(2) ^c δ _B 125.0(2) <i>J</i> _{AB} 215			F-5, -8, 146.0 (2) F-6, -7, 154.8 (2)		
(7)		218.3(2) <i>J</i> _{1,3(6,8)} 30	153.1(2)	δ _A 123.4(2) ^c δ _B 124.8 <i>J</i> _{AB} 215	198.6(2)		δ _A ' 131.6(2) ^c δ _B ' 133.5(2) <i>J</i> _{AB} ' 240	1.6	
(8)		218.1(2) <i>J</i> _{1,3(6,8)} 32	152.9(2)	δ _A 120.7(2) ^c δ _B 122.8 <i>J</i> _{AB} 225	197.6(2)		δ _A ' 125.3(2) ^c δ _B ' 128.3(2) <i>J</i> _{AB} ' 230	1.4	
(9a)		218.5(2) <i>J</i> _{1,3(6,8)} 28	153.4(2)	δ _A 121.6(2) ^c δ _B 122.9(2) <i>J</i> _{AB} 220	208.9(2)		δ _A ' 120.9(2) ^c δ _B ' 124.2(2) <i>J</i> _{AB} ' 225	2.0	
(10a)		218.0(2) <i>J</i> _{1,3(6,8)} 28	153.5(2)	123.0(4)	209.0(2)		123.0(4)	2.0	
(9b) or (10b)		218.1(2) <i>J</i> _{1,3(6,8)} 30	152.1(2)	δ _A 120.9(2) ^c δ _B 122.5(2) <i>J</i> _{AB} 230	208.2(2)		120.7(4)	3.9	
(10b) or (9b)		218.5(2) <i>J</i> _{1,3(6,8)} 30	150.2(2)	120.0(4)	207.8(2)		120.0(4)	3.9	
(11b)							F-1, -4 119.5(2) F-5, -8 141.3(2) F-6, -7, 151.2(2) <i>J</i> _{1,8(4,5)} 70	3.9	
(12)					193.4(2) <i>J</i> _{1,3(6,8)} 46		δ _A 127.5(2) ^c δ _B 129.6(2) <i>J</i> _{AB} 232	F-3, -6 146.6(2) F-4, -5 153.1(2)	1.5
		216.8(2)	153.0(2)	δ _A 121.3(2) ^c δ _B 122.3(2) <i>J</i> _{AB} 218	201.4(2)	124.3(4)	At C-10 and -12	3.8	
(16)							δ _A 117.0(2) δ _B 119.7(2) <i>J</i> _{AB} 256 At C-11 δ _A 132.6(1) δ _B 142.7(1) <i>J</i> _{AB} 254		
					199.1(2)	126.8(4)	C-10 and -12	F-3, -6 145.2(2) F-4, -5 150.1(2)	3.9
(17)					<i>J</i> _{1,3(6,8)} 40		δ _A 116.3(2) δ _B 121.4(2) <i>J</i> _{AB} 254 At C-11 δ _A 133.9(1) δ _B 142.9(1) <i>J</i> _{AB} 252		

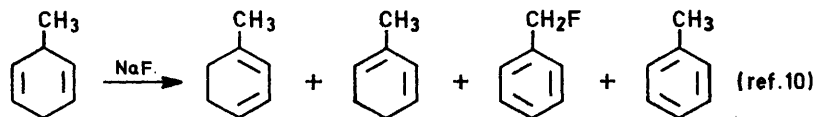
^a Shifts in p.p.m. from CFCl₃ or Me₄Si as reference; integrated intensities in parentheses; coupling constants in Hz. ^b Unmarked valencies to fluorine atoms. ^c Pseudo-AB systems.

originally adopted.² The structure (6) was assigned on the basis of elemental analysis and mass, i.r., u.v., and ¹⁹F n.m.r. spectra. Thus, the mass spectrum displayed a molecular ion at *m/e* 372 (8%) with the base peak, *m/e* 272, arising by elimination of the C₂F₄ bridge, a process supported by the observation of a strong metastable peak at *m/e* 198.9; the i.r. spectrum showed the expected -CF=CF- absorption at 1765 cm⁻¹ and a band at 1515 cm⁻¹ typical of a fluorinated aromatic ring; the u.v.

aromatic fluorine resonances which were assigned on the basis of the 36 Hz coupling between the tertiary fluorines at C-1 and -4 and the aromatic fluorines at C-5 and -8; pyrolysis of (6) gave perfluoronaphthalene, a result consistent with the assigned structure.

The formation of compound (6) in yields up to 18% deserves comment, since it must have arisen from triene (5) by either sodium fluoride-catalysed or pyrolytic 1,2-elimination of fluorine; such reactions are not without

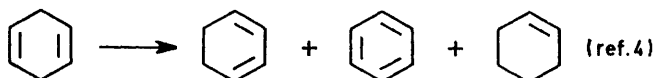
precedent. The pyrolysis of 3-methylheptafluorocyclohexa-1,4-diene over sodium fluoride in the range 410–530 °C resulted in a low conversion (<10%) into a mixture of the two isomeric dienes; pentafluoro(fluoromethyl)benzene, the product of dehydrofluorination and isomerization; and pentafluoro(methyl)benzene, the product of defluorination (Scheme 1).¹⁰ Indeed, in the



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SCHEME 1

earliest paper concerned with the thermal reactions of highly fluorinated cyclohexadienes the processes of isomerization, dehydrofluorination, and defluorination were reported together with a disproportionation reaction.⁴ For example, pyrolysis of perfluorocyclohexa-1,4-diene gave mixtures of the 1,3-isomer, hexafluorobenzene, and decafluorocyclohexene (Scheme 2).⁴ These



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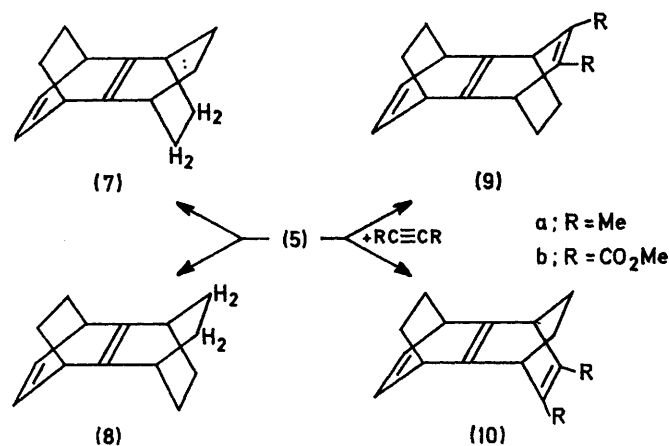
SCHEME 2

reactions were carried out by using mild steel or nickel tubes, 'aged' apparatus (presumably metal fluoride surfaces) favouring isomerization, and clean metal surfaces favouring defluorination. The isolation in this work of small but significant quantities of perfluorocyclohexene is consistent with a reaction involving elimination of fluorine, which subsequently adds to the diene to yield the observed olefin. In our case no products resulting from addition of fluorine to double bonds were observed; presumably fluorine if formed would be consumed in reactions with the resin binder in the pellets or the walls of the pyrolysis tube, and in practice small quantities of HF and SiF₄ were always observed in the products from these experiments.

The thermal reactions between the triene (5) and ethylene (210 °C), but-2-yne (125 °C), and dimethyl acetylenedicarboxylate (125 °C) gave in each case mixtures of the two possible Diels–Alder adducts. Both yield and conversion exceeded 90% for all these reactions. The isomers were separated by a combination of fractional crystallization and column chromatography as detailed in the Experimental section; ethylene gave an equimolar mixture of the isomers (7) and (8), but-2-yne gave the adducts (9a) and (10a) in a 3:1 molar ratio, respectively, and dimethyl acetylenedicarboxylate was marginally more discriminating giving the isomers (9b) and (10b) in a 5:1 molar ratio although in this case it was not possible to assign unequivocally the isomer stereochemistries (see later). All the compounds (7)–

(10) showed ¹⁹F n.m.r. signals characteristic of the octafluorobicyclo[2.2.2]oct-2-ene unit¹ (Table 1; unit labelled α), demonstrating that this structural feature had remained intact, the remainder of the ¹⁹F n.m.r. spectrum being consistent with the presence of a new –CF₂·CF₂– bridge and two new tertiary fluorines. Elemental analysis and molecular weight measurements

(mass spectrometry) confirmed the 1:1 adduct nature of the products, and double-bond stretching frequencies were observed at the appropriate frequencies in the i.r. spectra in all cases. The mass spectra of the adducts (7)–(10) all had base peaks corresponding to the elimination of two molecules of tetrafluoroethylene; on pyrolysis, however, only (9) and (10) eliminated two molecules of tetrafluoroethylene to give the appropriate naphthalene derivatives (11). Pyrolysis of the adducts (7) and (8) resulted in the elimination of only one molecule of tetrafluoroethylene and the formation of the ethanotetralin (12), identified on the basis of elemental analysis, ¹⁹F n.m.r. spectroscopy (Table 1), and appropriate mass, i.r., and u.v. spectra. Heating compound (12) at temperatures up to 750 °C had no effect; this contrasts with the behaviour of the Diels–Alder adduct of ethylene with perfluorocyclohexa-1,3-diene, which eliminates ethylene on pyrolysis.¹¹ The assignment of



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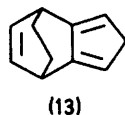
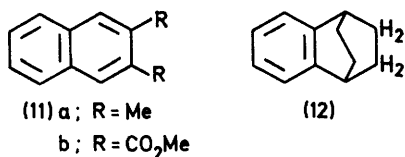
SCHEME 3

stereochemistries to the pairs of isomers (7) and (8), (9a) and (10a), and (9b) and (10b) presents the same kinds of difficulties that were encountered with the adducts of perfluorotricyclo[5.2.2.0^{2,7}]undeca-2,5,8-triene (13).¹ The problem is that of deciding whether the bridging difluoromethylene groups in the adducts are in

¹⁰ A. B. Clayton, W. J. Feast, R. Stephens, and J. C. Tatlow, *J. Chem. Soc. (C)*, 1971, 1183.

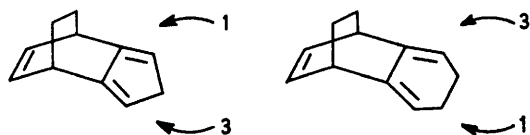
¹¹ W. J. Feast, W. K. R. Musgrave, and R. G. Weston, *J. Chem. Soc. (C)*, 1971, 937.

a *syn*- or an *anti*-relationship to one another. If they are in a *syn*-relationship then the close proximity in space of some of the fluorine atoms in the bridges can result in detectable spin-spin interaction in the ^{19}F n.m.r. spectra. In the work with the triene (13) this method allowed a fairly unambiguous assignment of



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stereochemistries, and it was also noted that the isomers with fluorinated bridging groups in a *syn*-relationship had considerably longer g.l.c. retention times than the *anti*-isomers. The statement in Part 6¹ that isomer structures could be deduced on the basis of comparisons of crystalline form is clearly an error and should be disregarded. The ^{19}F n.m.r. analysis and g.l.c. retention time comparisons used previously can be applied in the present work. Thus, in the spectrum of (7) a coupling constant of 37 Hz is observed in one limb of both pseudo-AB systems arising from the $-\text{CF}_2\cdot\text{CF}_2-$ bridges; this may be assigned to a through-space spin-spin interaction between adjacent fluorines in the *syn*-related bridges; isomer (7) also has the longer g.l.c. retention time as required if the analogy with the earlier work is to be maintained. The approach outlined above does not provide a clear stereochemical assignment for the acetylene adducts (9) and (10), although in the case of the adducts (9a) and (10a) the difference in g.l.c. retention times between the two isomers was large, allowing a provisional assignment on this basis which was confirmed by X-ray crystallography.¹² The reactivity of compound (5) in Diels-Alder additions appears to be qualitatively similar to that of compound (13), both (5) and (13) being more reactive than perfluorocyclohexa-1,3-diene (1).¹³ The selectivity of addition to the

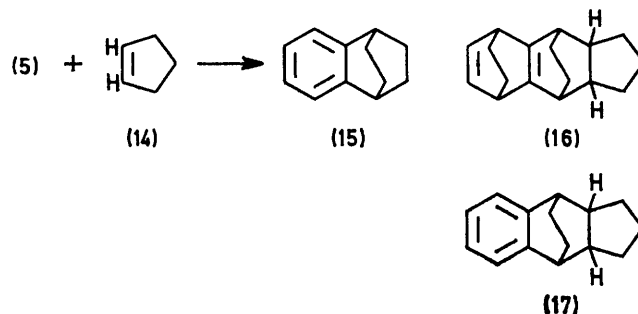


Diels-Alder additions of but-2-yne to the trienes (5) and (13)
All unmarked bonds to fluorine

trienes (5) and (13) differs; in the case of addition of but-2-yne to triene (5), addition from the same side as the $-\text{CF}_2\cdot\text{CF}_2-$ bridge was preferred by a factor of 3 : 1, whereas for the triene (13) the situation is exactly reversed (see Figure). Product ratios such as these

indicate very small differences between the free energies of the transition states leading to the isomeric adducts and hardly justify elaborate explanations; however the absence of a high stereoselectivity is in line with Jacobson's conclusion that secondary orbital interaction with a neighbouring non-conjugated double bond is not an important determinant of stereochemical control in Diels-Alder reactions.¹⁴

The triene (5) also underwent Diels-Alder reaction with 1*H*,2*H*-hexafluorocyclopentene (14), underlining its reactivity in cycloadditions. The reaction was carried out in a Pyrex ampoule at 335 °C with a large excess of the olefin to try to ensure that the reagents remained in the liquid phase. Under these conditions some decomposition occurred and the initially formed adduct (16) lost one $-\text{CF}_2\cdot\text{CF}_2-$ bridge to give the major product (17) (Scheme 4). Small amounts of the ethano-tetralin (15), an isomer of the triene (5), were also isolated, the probable derivation of this compound being stepwise addition of tetrafluoroethylene to (5) followed by elimination of the $-\text{CF}_2\cdot\text{CF}_2-$ bridge originally present



All unmarked bonds to fluorine
SCHEME 4

to generate the aromatic ring, rather than an isomerization of (5). The structures of compounds (16) and (17) follow straightforwardly from their ^{19}F n.m.r. (Table I), mass, i.r., and u.v. spectra. In principle there are four possible Diels-Alder adducts of (14) with (5) and although molecular models suggest the normally favoured *endo*-approach of (14) to the diene moiety in (5) would suffer considerable steric hindrance, the four possible adduct structures appear to be acceptable on steric grounds. However under the conditions used only one adduct was isolated, and it has not proved possible to assign its stereochemistry; likewise only one of the two possible stereoisomers of (17) was isolated from this experiment and it was not possible to decide whether the cyclopentane ring was *syn* or *anti* with respect to the aromatic ring on the available evidence.

In summary, the synthesis of perfluorotricyclo-[6.2.2.0^{2,7}]dodeca-2,6,9-triene (5) has been re-examined and some improvement in overall yield obtained. The diene moiety of (5) has been shown to be reactive in

¹² H. M. M. Shearer, in preparation.

¹³ L. P. Anderson, W. J. Feast, and W. K. R. Musgrave, *J. Chem. Soc. (C)*, 1969, 211.

¹⁴ B. M. Jacobson, *J. Amer. Chem. Soc.*, 1973, **95**, 2579.

Diels–Alder additions, its increased reactivity in comparison with perfluorocyclohexa-1,3-diene probably being a consequence of the rigidly *cis*-coplanar configuration imposed.

EXPERIMENTAL

I.r., u.v., mass, and n.m.r. spectra were recorded with a Perkin-Elmer 457 grating spectrophotometer, a Unicam SP 800 spectrophotometer, an A.E.I. MS9 spectrometer or a V.G. Micromass 12b instrument, and a Varian A56/60 (56.46 MHz for ^{19}F ; 60.0 MHz for ^1H) or Bruker HX 90E (84.67 MHz for ^{19}F ; 90 MHz for ^1H) spectrometer, respectively. G.l.c. was performed on a variety of instruments with di-*n*-decyl phthalate, silicone oil, or 2-cyanoethylmethylsilicone as stationary phases and hot-wire, flame ionization, or gas density balance detectors; where mixture compositions are quoted they were computed from integrated peak areas by using the gas density balance detector or from pre-calibrated response factors. A conventional vacuum system incorporating a rotary oil pump, mercury diffusion pump, and mercury manometers was used to manipulate and meter volatile compounds.

2H,7H-Hexadecafluorotricyclo[6.2.2.0^{2,7}]dodec-9-ene (3).—This was prepared by the Diels–Alder addition of 1H,2H-octafluorocyclohexene (2) to octafluorocyclohexa-1,3-diene (1). In a series of 30 experiments conditions were established that gave considerably better yields than the 17% reported previously.² Some of the results are recorded in Table 2 below to illustrate the generalizations drawn from this series of experiments. Thus, increasing the duration

TABLE 2
Synthesis of the adduct (3)

Run	Reagents		Ampoule vol. (ml)	Time (h)	Temp. (°C)	Yields	
	(1) (mmol)	(2) (mmol)				% (3) w.r.t. (2)	% (4) w.r.t. (1)
a	27	27	100	35	335	13	14
b	30	26	100	59	340	22	18
c	35	30	100	80	340	27	12
d	36	28	100	112	355	33	12
e	89	58	150	70	345	31	23
f	134	100	150	72	345	30	21

(*cf.* runs b and c) and temperature (*cf.* runs a—d) of reaction increases the yield of (3); unfortunately both the amount of intractable decomposition product and the extent of isomerization of octafluorocyclohexa-1,3-diene to its 1,4-isomer also increase with duration and temperature. These reactions were carried out in glass ampoules (Carius tubes) made from Pyrex tube (26 mm o.d., 3 mm wall) and sealed *in vacuo* (*ca.* 10⁻³ mmHg) after degassing reagents by freeze–thaw cycles; a small proportion of the ampoules exploded during the heating stage. Under these conditions the critical pressures of the reactants are probably exceeded, most of the reactants remaining in the liquid phase; consistent with this hypothesis, increasing the quantity of reactants per ampoule (*cf.* runs e and f) had no detectable effect on the product distribution. Experiments in which the reactants were heated in a stainless steel autoclave gave (3) in only *ca.* 6% yield and high conversions of (1) and (2) into hexa- and 1,2,3,4-tetra-fluorobenzenes, essentially the same result being obtained with a new or previously ‘aged’ autoclave. This result precluded an investigation of the effect of higher pressures on the reaction. Conditions specified in run f gave reasonable

conversions into products, a good mass recovery (*ca.* 95%), and a relatively small amount of diene isomerization (*ca.* 4%); the diene (1) and the olefin (2) were recovered by distillation and recycled; the accumulated mixtures of adducts (3) and dimers (4) were separated by fractional distillation under reduced pressure (concentric tubes column; Fischer ‘Spaltrohr-System’; Buchi model MMS 200), the dimers (4) boiling at 53 °C and 10 mmHg, and the adducts (3) at 58 °C and 10 mmHg.

Perfluorotricyclo[6.2.2.0^{2,7}]dodeca-2,6,9-triene (5).—This was prepared by dehydrofluorination of the adduct (3). Several different techniques were examined in an attempt to improve the reported yield.

(a) *Use of aqueous potassium hydroxide.* This heterogeneous reaction proved difficult to control. After a long series of experiments the technique adopted was essentially that described previously. However, in addition to duration of reflux and concentration of reagents, the scale of reaction and the manner in which the heat was applied to the mixture were significant determinants of the course of reaction. Fairly reproducible results were obtained when the adduct (3) (12–15 g) was mixed with aqueous potassium hydroxide (*ca.* 80 ml; *ca.* 60% w/w) and heated under reflux at *ca.* 160 °C for 10–20 min. The exact duration of the reflux period was determined by observation: as the reaction proceeded the reflux rate increased and the solution darkened, and the point at which the reaction was quenched was determined empirically. Under these conditions material balances of *ca.* 80% were generally obtained, with yields in the range 20–30% but occasionally reaching the extremes of 2 and 48%. The triene (5) was recovered by fractional distillation (concentric tubes column), boiling at 53 °C and 10 mmHg.

(b) *With molten potassium hydroxide.* The adduct (3) (10.7 g) was injected over 15 min into a chamber swept by a stream of dry nitrogen and maintained at 200 °C. The nitrogen stream was bubbled through fluid potassium hydroxide (B.D.H. laboratory reagent grade; *ca.* 300 g) maintained at 260 °C and then passed through a glass trap cooled in liquid air. The system was swept with nitrogen for a further 0.5 h after completion of addition of (3); only unchanged (3) (0.3 g) was recovered from the trap and the potassium hydroxide became black. Variations in temperature, rate of addition, nitrogen flow rate, and configuration of the bubbling apparatus gave essentially the same result.

(c) *With potassium hydroxide in benzene.* The adduct (3) (0.2 g), benzene (2.1 g) and powdered potassium hydroxide (B.D.H. laboratory reagent; fresh sample opened and powdered in a dry glove box; 0.05 g) were mixed at room temperature. The dark brown mixture was refluxed briefly, and became black. G.l.c. analysis of the organic product revealed only benzene. Variation of relative proportions of reagents and benzene gave similar results, either complete or partial degradation of (3) but never any evidence for the presence of (5).

(d) *With anion-exchange resin.* The adduct (3) (0.1 g) and Amberlite IRA 400 (OH⁻) resin (dried at 60 °C and 10⁻³ mmHg for 10 h; 0.4 g) were sealed *in vacuo* in a Pyrex ampoule (*ca.* 3 ml) and heated at 60 °C for 4 h. The adduct (3) was recovered unchanged. The same result was obtained when the experiment was repeated with the inclusion of benzene (1 ml).

(e) *With sodium fluoride.* (i) The adduct (3) (1.0 g) was heated under reflux (b.p. 174 °C) with dry sodium fluoride

(0.6 g) for 1 h. There was no detectable reaction, the adduct (3) being recovered quantitatively.

(ii) The adduct (3) (0.82 g) and dry powdered sodium fluoride were sealed *in vacuo* in a Pyrex ampoule and heated at 275 °C for 1 h. The only characterizable organic material recovered was (3) (<0.01 g); the residual material in the ampoule was a fine water-insoluble powder.

(iii) The adduct (3) was injected into a chamber swept by dry nitrogen and maintained at 220 °C. The stream of gas was passed over sodium fluoride pellets (Thompson and Capper Ltd.; 1 g pellets) packed in a silica tube (2.0 cm i.d., 55 cm long) which was heated in an electric furnace. The organic products were trapped from the nitrogen stream in glass traps cooled in liquid air. The detailed outcome of the process depended on the furnace temperature, the rate of addition of (3), the carrier gas flow rate, and the 'age' of the sodium fluoride pellets. Conversions decreased with time as the pellets became coated with a dark film. The accumulated product from several runs was fractionally distilled (concentric tubes column) to give: (a) perfluorotricyclo[6.2.2.0^{2,7}]dodeca-2,6,9-triene (5); (b) the adduct (3); (c) *perfluoro-1,4-dihydro-1,4-ethanonaphthalene* (6), b.p. 63 °C at 10 mmHg, containing perfluoro-1,2-dihydronaphthalene (*ca.* 2%); and a pot residue of (6) containing perfluoronaphthalene (*ca.* 10%). Compound (6) was obtained pure by recrystallization from light petroleum (b.p. 40–60 °C) at –20 °C (Found: F, 61.1%; M^+ , 372. $C_{12}F_{12}$ requires F, 61.3%; M , 372) as a solid, m.p. 30–31 °C, ν_{\max} 1 765 (CF=CF) and 1 515 cm^{-1} (fluorinated aromatic ring), λ_{\max} 253sh (ϵ 3 200), 260 (3 600), 269sh (3 000), 294 (2 700), and 302sh nm (2 300). The results in Table 3 were obtained at a carrier gas flow rate of 1 l h⁻¹

TABLE 3

Dehydrofluorination of the adduct (3) over sodium fluoride pellets

Run	(3) (g)	Rate of addition (g h ⁻¹)	Product recovered (g)	(5) (%)	(6) (%)
A	2.0	0.7	0.9	20	15
B	2.2	1.2	1.2	28	18
C	2.2	2.0	1.4	24	12

and a furnace temperature of 365 °C. Higher temperatures resulted in relatively more perfluoro-1,2-dihydronaphthalene and perfluoronaphthalene, which made purification of (5) and (6) difficult; milder conditions gave much lower conversions of (3) into (5) and (6).

Diels-Alder Reactions of Perfluorotricyclo[6.2.2.0^{2,7}]dodeca-2,6,9-triene (5).—(a) *With ethylene*. A mixture of the triene (5) (1.52 g, 3.71 mmol) and ethylene (5.88 mmol) was sealed *in vacuo* in a Pyrex ampoule (100 ml), which was heated at 210 °C for 34 h to give: (i) ethylene (2.34 mmol), (ii) a liquid (0.08 g, 0.19 mmol), shown by i.r. and g.l.c. to be the triene (5); and (iii) a white solid (1.42 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 crystallization from light petroleum (b.p. 60–80 °C) to give the two isomers of 4*H*,4*H*,5*H*,5*H*-tetradecafluorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-2(7),9-diene, (7) and (8). The isomer (8) with the shorter g.l.c. retention time (Found: C, 38.1; H, 0.9; F, 61.0%; M^+ , 438. $C_{14}H_4F_{14}$ requires C, 38.4; H, 0.9; F, 60.7%; M , 438) formed platelets, m.p. 92–93°, ν_{\max} 1 765 (–CF=CF–) and 1 645 cm^{-1} (C=C). The isomer (7) with the longer g.l.c. retention time (Found: C, 38.1; H, 1.0;

F, 61.0%; M^+ , 438) gave fine white needles, m.p. 135–136°, ν_{\max} 2 930 (CH₂), 1 755 (–CF=CF–), and 1 650 cm^{-1} (C=C).

(b) *With but-2-yne*. By the same procedure as in (a), the triene (5) (1.82 g, 4.54 mmol) and but-2-yne (0.326 g, 5.53 mmol) were heated in a Pyrex ampoule (100 ml) at 125 °C for 68 h to give: (i) unchanged but-2-yne, (ii) the triene (5) (0.09 g), and (iii) a white solid (1.93 g) shown by analytical g.l.c. to contain two components in the ratio 74 : 26. The major component (9a) was obtained pure by recrystallization from light petroleum (b.p. 60–80 °C); repeated recrystallization of the residue from acetone–light petroleum gave a pure sample of the minor component (10a). The major isomer of 4,5-dimethyltetradecafluorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-2,4,9-triene (9a) with the shorter g.l.c. retention time (Found: C, 41.1; H, 1.5; F, 57.1%; M^+ , 464. $C_{16}H_6F_{14}$ requires C, 41.4; H, 1.3; F, 57.3%; M , 464) formed needles, m.p. 127.5°, ν_{\max} 1 763 (–CF=CF–) and 1 640 cm^{-1} (C=C). The minor isomer (10a) with the longer retention time (Found: C, 41.1; H, 1.6; F, 57.0%; M^+ , 464) was obtained as needles, m.p. 118.5°, ν_{\max} 1 760 (–CF=CF–) and 1 640 cm^{-1} (C=C).

(c) *With dimethyl acetylenedicarboxylate*. By the same procedure as in (a), the triene (5) (2.20 g, 5.37 mmol) and dimethyl acetylenedicarboxylate (5.60 mmol) were heated in a Pyrex ampoule (100 ml) at 125 °C for 72 h to give: (i) unchanged triene (5) (0.20 g) and (ii) a discoloured solid (2.65 g) shown by analytical g.l.c. to contain starting materials and traces of impurities (totalling *ca.* 5% of the mixture) and two products in the ratio 16 : 84, with the major product having the longer retention time. The major product was obtained pure by recrystallization from chloroform at –20 °C; the residue from this recrystallization was predominantly (*ca.* 80%) the minor product, and a sample was obtained pure by column chromatography (silica; CHCl₃) and recrystallization from light petroleum (b.p. 60–80 °C) at –20 °C. The two products are the isomers of dimethyl tetradecafluorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-2,4,9-triene-4,5-dicarboxylate (9b) and (10b), formed in a total yield of *ca.* 90%. The major isomer (Found: C, 39.1; H, 1.1; F, 48.2%; M , 552) had m.p. 185°, ν_{\max} 2 975 (CH₃), 1 770 (–CF=CF–), 1 750 and 1 730 (C=O), and 1 670 and 1 635 cm^{-1} (C=C). The minor isomer (Found: C, 39.4; H, 0.9; F, 48.6%; M^+ , 552) had m.p. 148°, ν_{\max} 2 970 (CH₃), 1 765 (–CF=CF–), 1 745 (C=O), and 1 660 and 1 640 cm^{-1} (C=C).

(d) *With 1*H*,2*H*-hexafluorocyclopentene* (14). By the same procedure as in (a), the triene (5) (0.743 g, 1.05 mmol) and 1*H*,2*H*-hexafluorocyclopentene (14) were heated in a Pyrex ampoule (*ca.* 1 ml) for 25 h at 335 °C. The contents of the ampoule were washed with water and transferred *in vacuo* from P₂O₅ to give a liquid (0.71 g) which was separated into: (i) a volatile fraction (0.18 g), primarily the olefin (11) (by i.r. and g.l.c.); and (ii) a liquid fraction (0.53 g) which was shown by a combination of analytical g.l.c., g.l.c.–mass spectrometry, and preparative g.l.c. to consist of (a) 1*H*,2*H*-hexafluorocyclopentene (14) (8%); (b) the triene (5) (5%); (c) perfluorotricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (15) (3%) (i.r. spectrum);¹⁵ (d) perfluoro-1,2-dihydronaphthalene (3%); (e) 4*H*,8*H*-eicosafluoropentacyclo[6.5.2.2^{3,6}.0^{2,7}.0^{9,13}]heptadeca-2(7),4-diene

¹⁵ W. J. Feast, R. R. Hughes, and W. K. R. Musgrave, *in preparation*; R. R. Hughes, Ph.D. Thesis, Durham University, 1975.

(16) (7%), M^+ 586, a white solid, m.p. 86 °C, ν_{\max} 1 768 cm^{-1} ($-\text{CF}=\text{CF}-$); and (f) 9H,13H-hexadecafluorotetracyclo-[6.5.2.0^{2,7}.0^{9,13}]pentadeca-2,4,6-triene (17) (74%) (Found: F, 62.3%; M^+ , 486. $\text{C}_{15}\text{H}_2\text{F}_{16}$ requires F, 62.5%; M , 486), a white solid, m.p. 84°, ν_{\max} 1 505 cm^{-1} (fluorinated benzene ring), λ_{\max} 265 nm (ϵ 850).

Vacuum Pyrolyses of the Diels-Alder Adducts of the Triene (5).—Pyrolyses were carried out in the manner described previously.^{11,12}

(a) An equimolar mixture of the ethylene adducts (7) and (8) (0.679 g, 1.59 mmol) was pyrolysed at 620 °C and 10⁻³ mmHg to give (i) tetrafluoroethylene (1.36 mmol), identified by i.r. and mass spectrometry, and (ii) a solid (0.488 g) shown by g.l.c. to be a single product contaminated with small amounts of (7) and (8). Recrystallization from light petroleum (b.p. 60–80 °C) gave pure 9H,9H,10H,10H-decafluorotricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (15) (Found: C, 42.8; H, 1.4; F, 56.5%; M^+ , 338. $\text{C}_{12}\text{H}_4\text{F}_{10}$ requires C, 42.6; H, 1.2; F, 56.3%; M , 338), a white solid, m.p. 89°, ν_{\max} 2 920 (CH_2) and 1 510 cm^{-1} (fluorinated benzene

ring), λ_{\max} 263 nm (ϵ 850). Heating the product (15) at temperatures up to 750 °C resulted in no further degradation.

(b) An equimolar mixture of the but-2-yne adducts (9a) and (10a) (0.058 g, 0.126 mmol) was heated at 650 °C and 10⁻³ mmHg to give 2,3-dimethylhexafluoronaphthalene (16a) (0.028 g, 0.106 mmol, 84%), identified by its i.r. and mass spectra and m.p.

(c) The major dimethyl acetylenedicarboxylate adduct (9b) or (10b) (0.540 g, 0.98 mmol) was heated at 650 °C and 10⁻³ mmHg to give: (i) tetrafluoroethylene, contaminated with traces of SiF_4 (1.05 mmol total gas), and (ii) dimethyl hexafluoronaphthalene-2,3-dicarboxylate (16b) (0.260 g, 0.74 mmol, 76%) (Found: C, 47.9; H, 2.0; F, 32.7%; M^+ , 352. $\text{C}_{14}\text{H}_6\text{F}_6\text{O}_4$ requires C, 47.7; H, 1.8; F, 32.4%; M , 352), white crystals, m.p. 107–108° [from light petroleum (b.p. 60–80 °C)], ν_{\max} 2 970 (CH_2), 1 745 and 1 728 ($\text{C}=\text{O}$), and 1 530 cm^{-1} (fluorinated aromatic), λ_{\max} 340 (ϵ 3 900), 327 (2 900), 295 (1 900), 283 (2 500), and 273 nm (2 300).

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