Diels–Alder Reactions of Polyfluorocyclohexa-1,3-dienes. Part V.[1] Addition of Cycloalkenes to Octafluorocyclohexa-1,3-diene and Dehydrofluorination of Some of the Adducts

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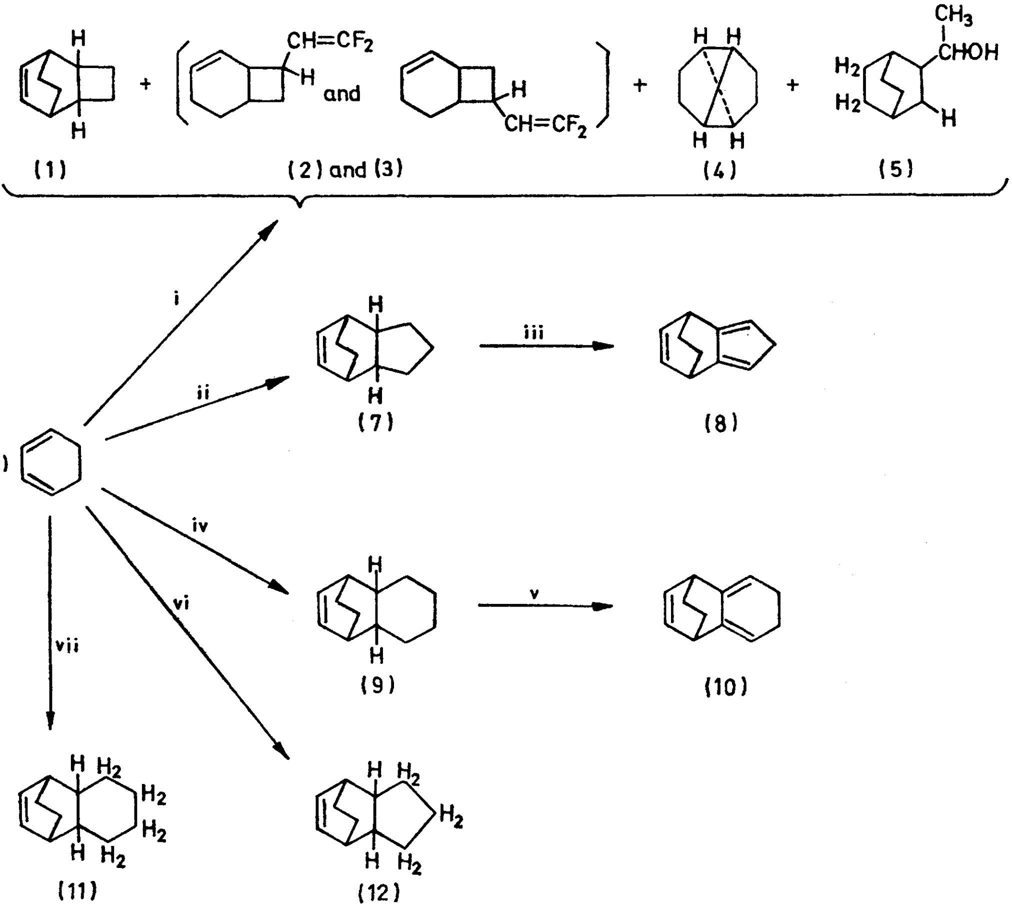
Perfluorocyclohexa-1,3-diene (6) gives the expected Diels–Alder adducts with cyclohexene, cyclopentene, 1*H*,2*H*-octafluorocyclohexene, 1*H*,2*H*-hexafluorocyclopentene, and 1*H*,2*H*-tetrafluorocyclobutene; in the case of 1*H*,2*H*-tetrafluorocyclobutene two 2,2-difluorovinyldecafluorobicyclo[2,2,2]oct-2-enes and the dimer, 3,3,4,4,7,7,8,8-octafluorotricyclo[3,3,0,0^{2,6}]octane (4), were also isolated. Dehydrofluorination of the adducts formed from 1*H*,2*H*-octafluorocyclohexene and 1*H*,2*H*-hexafluorocyclopentene gave perfluorotricyclo[6,2,2,0^{2,7}]-dodeca-2,6,9-triene (10) and perfluorotricyclo[5,2,2,0^{2,6}]undeca-2,5,8-triene (8), respectively.

ALTHOUGH many Diels–Alder additions to polyfluorocyclohexa-1,3-dienes have been reported,[1-6] there are few examples involving cyclic dienophiles. As part of a general study of the Diels–Alder reactions of fluorinated dienes[1-3,5] we have examined the reactions between perfluorocyclohexa-1,3-diene (6) and five cyclic olefins.



SCHEME 1 Unmarked bonds are to fluorine atoms

Reagents: i, 1*H*,2*H*-tetrafluorocyclobutene; ii, 1*H*,2*H*-hexafluorocyclopentene; iii, molten KOH; iv, 1*H*,2*H*-octafluorocyclohexene; v, aq. KOH; vi, cyclopentene; vii, cyclohexene

The thermal reactions between the diene (6) and 1*H*,2*H*-tetrafluorocyclobutene, 1*H*,2*H*-hexafluorocyclopentene, 1*H*,2*H*-octafluorocyclohexene, cyclopentene, and cyclohexene all gave 1 : 1 adducts. In the case of 1*H*,2*H*-tetrafluorocyclobutene three 1 : 1 adducts [(1), (2), and (3)] were isolated, together with a dimer of

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[1] Part IV, W. J. Feast, W. K. R. Musgrave, and R. G. Weston, *J. Chem. Soc.* (*C*), 1971, 1547.

[2] R. D. Chambers, W. K. R. Musgrave, and D. A. Pyke, *Chem. and Ind.*, 1965, 564.

[3] L. P. Anderson, W. J. Feast, and W. K. R. Musgrave, *J. Chem. Soc.* (*C*), 1969, 211, 2559.

[4] W. B. Hollyhead, R. Stephens, J. C. Tatlow, and W. T. Westwood, *Tetrahedron*, 1969, **25**, 1777.

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

[6] R. E. Banks, L. E. Birks, M. Bridge, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1970, 2539.

1*H*,2*H*-tetrafluorocyclobutene (4) and mixtures of isomers of 1 : 1 adducts of diene (6) and the elements of diethyl ether (present as an impurity in the starting material). Diels–Alder addition reactions with the diene (6) give rise to the 2,3-substituted octafluorobicyclo[2,2,2]oct-5-ene unit, which is readily identified by its ^{19}F n.m.r. spectral parameters;[3,6] the typical tertiary, vinylic, and bridging $CF_2{\cdot}CF_2$ fluorine resonances present in 1 : 1 adducts (1), (7), (9), (11), and (12) (see Table) consequently identify them as the expected products of 1,4-cycloaddition.

^{19}F and ^{1}H N.m.r. spectral parameters[a]

Compound[b]	Tertiary F	Vinylic F		CF_2	Tertiary H	CH_2
(1)	202·4 (2)	149·7 (2)		127·2 (4)[c]	3·47	
			δ_A	108·1		
			δ_B	123·6		
			J_{AB}	226		
(7)	205·7 (2)	150·2 (2)		128·0 (4)[c]	3·25	
			δ_A	116·2 (2)		
			δ_B	124·1 (2)		
			J_{AB}	258		
			$\delta_{A'}$	132·1 (1)		
			$\delta_{B'}$	144·1 (1)		
			J_{AB}	258		
(9)	206·4 (2)	149·7 (2)		128·6 (4)[c]	3·2	
			δ_A	122·9 (2)		
			δ_B	133·3 (2)		
			J_{AB}	270		
			$\delta_{A'}$	111·9 (2)		
			$\delta_{B'}$	120·3 (2)		
			J_{AB}	270		
(11)[d]	208·1 (2)	151·5 (2)		128·5 (4)[c]	2·4 (2)	1·65 (8)
(12)	205·0 (2)	151·1	δ_A	125·3 (2)[c]	2·8 (2)	1·75 (6)
			δ_B	128·0 (2)[c]		
			J_{AB}	228		

[a] Shifts are in p.p.m. from internal $CFCl_3$ or external Me_4Si and refer to centres of broad bands or unresolved multiplets. [b] Neat liquids. [c] Bridging CF_2–CF_2. [d] Solution in CCl_4.

Only one stereoisomer of each of these 1,4-cycloaddition products was isolated, and this is presumed to be the *endo*-isomer by analogy with the two examples where the stereochemistry of Diels–Alder addition to perfluorocyclic dienes has been unambiguously established;[6,7] examination of Courtauld space-filling molecular models also supports the assignment of *endo*-stereochemistry to these adducts. Both hydrocarbon olefins reacted readily at 208° giving 81 and 96% of adducts (11) and (12), respectively. The hydrofluorocarbon olefins were much less reactive; at 300° or above yields of adducts (1) and (9) from the four- and six-membered ring olefins were less than 20% and that of adduct (7), from the five-membered ring dienophile was 70%. The low yield of 1,4-adduct from 1*H*,2*H*-tetrafluorocyclobutene is accounted for by the intervention of alternative competing reaction pathways. The lower yields of compounds (7) and (9) as compared to (12) and (11) are qualitatively as would be expected for reactions with 'inverse electron demand',[8] the olefins carrying the most electronegative substituents being the least reactive with the 'electron poor' diene (6).

Further, the yields of adducts from five-membered ring dienophiles are greater than the yields of adducts from the analogous six-membered ring dienophiles, *i.e.* the yield of compound (7) is greater than that of (9), and that of (12) is greater than that of (11). A possible explanation of these differences is that formation of adducts (7) and (12) involves the introduction of very little conformational strain, as the cyclopentane ring can maintain its planarity in the adduct, whereas in the formation of adducts (9) and (11) the reactant cyclohexene, presumably in a chair-like conformation,[9] has to assume the higher energy skew-boat or boat form in the adduct, since the C-2 and C-7 substituents are fixed in an eclipsed conformation. The greater difference in yields for the hydrofluorocarbon dienophiles is a consequence of the more restricted conformational mobility and/or the greater steric strain in the adduct (9). Heating pure compound (7) and pure (9) for prolonged periods at the temperature at which they were formed showed that although the rate of the retro-Diels–Alder reaction was slow at this temperature it was faster for (9) than for (7), which is consistent with the former adduct being the more sterically strained of the two.

The reaction of 1*H*,2*H*-tetrafluorocyclobutene with the diene (6) gave a complex product, which was separated into its components by preparative gas chromatography. The major product was the expected Diels–Alder adduct (1); the next most abundant products, (2) and (3), were also 1 : 1 adducts, as shown by mass spectroscopy and elemental analysis; however it was not possible to define their structures completely. The mass spectra of both compounds (2) and (3) displayed low intensity parent ions and base peaks at m/e 126 ($C_4H_2F_4^+$), in the light of which it seemed probable that the $C_4H_2F_4$ of the tetrafluorocyclobutene was retained intact in the adduct. The ^{1}H n.m.r. spectra of adducts (2) and (3) both showed two distinct signals, one a doublet of doublets (sharp lines) and the other an extensively coupled broad signal. The ^{19}F n.m.r. spectra indicated a lack of symmetry in both adducts, and in both cases included two low-field resonances which showed coupling only with each other and with the lower field of the two proton signals; the rest of the ^{19}F n.m.r. spectra of adducts (2) and (3) showed, in both cases, two tertiary and two vinylic fluorine resonances and three difluoromethylene signals. Taken together the data establish a 2,2-difluorovinyldecafluorobicyclo[4,2,0]oct-2-ene structure for both (2) and (3); however it is not possible to decide whether the difluorovinyl substituent occupies the 7- or the 8-position or to define its stereochemical relationship to the rest of the molecule. The i.r. spectrum supports the structural assignment, showing the two required olefinic absorptions at 1765 (CF=CF) and 1755 cm^{-1} ($CH{=}CF_2$),[10] and the presence of hydrogen atoms at both saturated (2975 cm^{-1}) and unsaturated (3100 cm^{-1}) sites.

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[7] R. E. Banks, L. E. Birks, and R. N. Haszeldine, *J. Chem. Soc.* (*C*), 1970, 201.

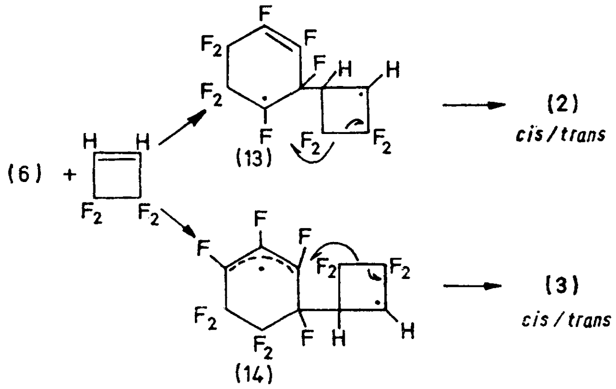
[8] J. Sauer, *Angew. Chem. Internat. Edn.*, 1966, **5**, 211; 1967, **6**, 16.

[9] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, ch. 8.

[10] R. E. Putnam, J. L. Anderson, and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1961, **83**, 386.

Adducts (2) and (3) could be formed in several ways. A [2 + 2] cycloaddition between the diene (6) and 1,1,4,4-tetrafluorobuta-1,3-diene formed by ring opening of 1*H*,2*H*-tetrafluorocyclobutene can be ruled out, since although the butadiene can be formed from the cyclobutene the reaction occurs only at high temperature and low pressure (550—750° and 5—25 mmHg) and requires immediate quenching of the product,[11] and it is well established that the equilibration between fluorinated dienes and cyclobutenes favours the butene under our reaction conditions.[12]

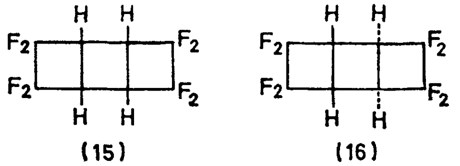
Further evidence which helps to exclude 1,1,4,4-tetrafluorobuta-1,3-diene as an intermediate in the formation of adducts (2) and (3) is the reported easy thermal polymerisation of this diene, which gives mixtures of dimer, trimers, and higher molecular weight materials;[10] none of these products were detected in this work although they would have been expected if 1,1,4,4-tetrafluorobuta-1,3-diene was an intermediate. Adducts (2) and (3) must consequently arise either through the intermediacy of diradicals (13) and/or (14) as shown in Scheme 2; or alternatively *via* a [2π + 2π + 2σ] cycloaddition,[13] involving one π-bond of the diene and both the π-bond and the C(3)–C(4) σ-bond of the cyclobutene.



Scheme 2

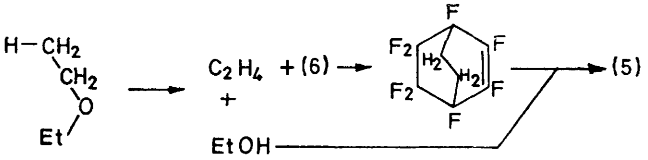
The dimer (4) isolated from this reaction, and also formed as the sole product on heating 1*H*,2*H*-tetrafluorocyclobutene, showed no olefinic stretching vibrations in either its i.r. or its Raman * spectrum, and is consequently saturated and tricyclic; further it has a highly symmetrical structure since the ^{19}F and ^{1}H n.m.r. resonances are sharp singlets. Structure (4) is preferred over the alternatives (15) and (16), because the fluorine atoms in (15) and (16) are expected to be in sufficiently different environments to give rise to separate resonances or at least line broadening in the ^{19}F n.m.r. spectrum.

There is a precedent for structures analogous to (4): the thermal dimerisation of perfluorobuta-1,3-diene gives perfluorotricyclo[3,3,0,0^{2,6}]octane.[14] The mechanism of this dimerisation has been the subject of speculation[15] but remains obscure. In relation to this, Putnam *et al.*[10] found no saturated dimer in the product of thermal polymerisation of 1,1,4,4-tetrafluorobuta-1,3-diene. In view of the fact that the equilibrium between perfluorocyclobutene and perfluorobuta-1,3-diene favours the formation of the cyclobutene,[12] it may be that these saturated dimers are both formed from the cyclobutenes rather than the buta-1,3-dienes.



Scheme 3

There were several long-retained components from the reaction of 1*H*,2*H*-tetrafluorocyclobutene with the diene (6); they were not isolated in a pure state but were examined as mixtures. In each case the peak of highest mass in the mass spectrum corresponded to a 1 : 1 adduct of the diene (6) with the elements of diethyl ether. There was no double-bond stretching absorption in the i.r. spectrum, and the ^{19}F and ^{1}H n.m.r. spectra were consistent with the compounds being mixtures of isomers of 1,2,3,4,5,5,6,6-octafluoro-2-(1-hydroxyethyl)-bicyclo[2,2,2]octane (5). These products could be formed by pyrolytic elimination of ethylene from diethyl ether, formation of the adduct (17), and subsequent radical addition of ethanol. Their abundance in the product mixture was dependent on the amount of diethyl ether impurity in the 1*H*,2*H*-tetrafluorocyclobutene used initially, and it was felt that as minor products arising from impurities in starting material they did not merit detailed investigation.



Scheme 4

Adducts (7) and (9) were dehydrofluorinated to give the trienes (8) and (10), respectively. The dehydrofluorination method used was empirically established, the triene (8) being obtained in high yield by passing compound (7) through molten potassium hydroxide in a stream of nitrogen as carrier whereas the triene (10) was obtained in only moderate yield on heating and stirring the adduct (9) with aqueous 50% potassium hydroxide. Application of the molten potassium hydroxide technique to compound (9) gave only traces of the triene (10), with extensive decomposition. The appropriate conditions for dehydrofluorination clearly

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* Run on a Perkin-Elmer LR-1, Laser-Excited Raman spectrometer using a Spectra-Physics 125 Laser; we thank Dr. C. J. Ludman for this measurement.

[11] J. L. Anderson, R. E. Putnam, and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1961, **83**, 382.

[12] E. W. Schlag and W. B. Peatman, *J. Amer. Chem. Soc.*, 1964, **86**, 1676.

[13] 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.

[14] 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.

[15] M. Prober and W. T. Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 598; J. D. Roberts and C. M. Sharts, *Org. Reactions*, 1962, **12**, 1.

depend on a combination of factors, including ease of loss of hydrogen fluoride, volatility of starting material and product, and stability of product to the reagent used. In the case of the adduct (1) this balance of factors must be particularly fine since all attempts at dehydrofluorination resulted in either recovery or decomposition of starting materials; no tractable product was obtained in several attempts under a variety of conditions. The trienes (8) and (10) had correct elemental analyses, and showed the expected mass and ^{19}F n.m.r. spectra.[16] No traces of monodehydrofluorination product from compounds (1), (7), or (9) were ever detected.

EXPERIMENTAL

General.—Techniques and apparatus were as described previously.[5] 1*H*,2*H*-Octafluorocyclohexene,[17] 1*H*,2*H*-hexafluorocyclopentene,[18] and 1*H*,2*H*-tetrafluorocyclobutene [19] were prepared by published routes. Perfluorocyclohexa-1,3-diene was prepared and purified as described previously.[3] Cyclohexene and cyclopentene (Koch–Light) were used without further purification. N.m.r. references were internal $CFCl_3$ and external Me_4Si unless otherwise stated.

Cycloadditions of Octafluorocyclohexa-1,3-*diene* (6) *with Cycloalkenes*.—(a) *With* 1H,2H-*octafluorocyclohexene*. In a typical experiment octafluorocyclohexa-1,3-diene (6) (7·54 g, 33·6 mmol) and 1*H*,2*H*-octafluorocyclohexene (5·38 g, 23·8 mmol) were heated at 330° for 31 h in a 90 ml Pyrex ampoule which had been sealed *in vacuo*. The product mixture was separated by conventional vacuum-line techniques to give: (i) a liquid mixture (7·08 g), shown by analytical gas chromatography and i.r. spectroscopy to consist of perfluorocyclohexa-1,3-diene (*ca.* 56%) and 1*H*,2*H*-octafluorocyclohexene (*ca.* 44%) with a trace of perfluorocyclohexa-1,4-diene; (ii) a liquid mixture (5·15 g) which was separated (column A, 120°) to give perfluorocyclohexa-1,3-diene (6) (0·28 g), 1*H*,2*H*-octafluorocyclohexene containing traces of perfluorocyclohexa-1,3-diene dimers (1·76 g), and 2H,7H-*hexadecafluorotricyclo*[6,2,2,0^{2,7}]-*dodec*-9-*ene* (9) (1·86 g, 4·13 mmol, 17·3%) [Found: C, 31·8; H, 0·6; F, 67·9%; *M* (mass spectrometry), 450. $C_{12}H_2F_{16}$ requires C, 32·0; H, 0·5; F, 67·5%; *M*, 450], b.p. 174°, $\nu_{max.}$ 2985 (C–H) and 1776 cm^{-1} (CF=CF); and (iii) an involatile solid residue (*ca.* 0·1 g).

Under more forcing conditions, for example 35 h at 350°, a greater proportion of the recovered diene was isomerised to the 1,4-isomer but the yield of compound (9) was not improved. Milder reaction conditions, for example 24 h at 235°, gave no detectable reaction.

(b) *With* 1H,2H-*hexafluorocyclopentene*. By the same procedure as in (a), perfluorocyclohexa-1,3-diene (6) (7·63 g, 34·0 mmol) and 1*H*,2*H*-hexafluorocyclopentene (5·86 g, 33·3 mmol), heated at 326° in an 80 ml Pyrex ampoule for 43 h, gave: (i) a liquid mixture (2·79 g), consisting of starting materials; (ii) 2H,6H-*tetradecafluorotricyclo*-[5,2,2,0^{2,6}]*undec*-8-*ene* (7) (9·38 g, 23·4 mmol, 70·2%) [Found: C, 33·3; H, 0·5; F, 66·9%; *M* (mass spectrometry), 400. $C_{11}H_2F_{14}$ requires C, 33·0; H, 0·5; F, 66·5%; *M*, 400], b.p. 153°, $\nu_{max.}$ 2994 (tertiary C–H) and 1773 cm^{-1} (CF=CF); and (iii) a trace of involatile black solid residue.

This addition was conveniently carried out on a larger scale in an aged stainless steel autoclave; for example, the diene (6) (22·06 g, 98·45 mmol) and 1*H*,2*H*,hexafluorocyclopentene (17·82 g, 101·2 mmol), heated in a 150 ml autoclave at 340° for 16 h, gave compound (7) (26·39 g, 66·0 mmol, 67%), a mixture of starting materials (8·23 g), and an involatile residue (0·9 g). Use of an autoclave with a clean metal surface results in a marginally lower yield of (7), together with substantial recoveries of unchanged olefin and hexafluorobenzene derived from (6) by defluorination at the metal surface.

Milder reaction conditions gave low yields of (7); for example, an equimolar mixture of the diene (6) and 1*H*,2*H*-hexafluorocyclopentene heated at 280° for 21 h gave only 14% of (7) together with unchanged starting materials.

(c) *With* 1H,2H-*tetrafluorocyclobutene*. By the same procedure as in (a), perfluorocyclohexa-1,3-diene (6) (3·57 g, 15·9 mmol) and 1*H*,2*H*-tetrafluorocyclobutene containing traces of diethyl ether (1·75 g, <13·9 mmol) heated at 295° in a 130 ml Pyrex ampoule for 42 h gave: (i) a gaseous fraction which was discarded; (ii) a liquid mixture (3·76 g); and (iii) an involatile yellow oil. Fraction (ii) was separated by preparative gas chromatography (column A, 108°) to give: (a) *cis*- or *trans*-7 or 8-(2,2-difluorovinyl)-7*H*- or 8*H*-decafluorobicyclo[4,2,0]oct-2-ene [(2) or (3)] (0·49 g, 1·4 mmol, *ca.* 10%) [Found: C, 34·0; H, 0·6; F, 65·1%; *M* (mass spectrometry), 350. Calc. for $C_{10}H_2F_{12}$: C, 34·3; H, 0·6; F, 65·1%; *M*, 350], a colourless liquid, b.p. 132°, $\nu_{max.}$ 3100 (=CH–), 2975 (tertiary C–H), 1765 (CF=CF), and 1755 cm^{-1} (CH=CF$_2$), ^{19}F n.m.r. (ext. $CFCl_3$) resonances at 210·1 (1F, m) and 222·6 (1F, m) (tertiary F), 149·6 (1F, s) and 155·8 (1F, s) (vinylic F), 129·5 (2F, m), 127·4 (2F, m), 113·1 (2F, m), and 80·0 (1F, d, *J* 25 Hz) and 85·4 p.p.m. (1F, dd, *J* 25 and 21 Hz) (CH=CF$_2$); the ^1H n.m.r. signals consisted of a doublet of doublets (sharp lines; *J* 21 and 10 Hz) overlapping with a broad poorly resolved band, the whole spectrum being centred at 3·75 p.p.m.; (b) *cis*- or *trans*-7*H*- or 8*H*-decafluorobicyclo[4,2,0]oct-2-ene [(2) or (3)] (0·36 g, 1·03 mmol, *ca.* 8%) [Found: C, 34·0; H, 0·6; F, 65·4%; *M* (mass spectrometry), 350. Calc. for $C_{10}H_2F_{12}$: C, 34·3; H, 0·6; F, 65·1%; *M*, 350], a colourless liquid, $\nu_{max.}$ 3100 (=CH–), 2975 (tertiary C–H), 1765 (CF=CF), and 1755 cm^{-1} (CH=CF$_2$), ^{19}F n.m.r. (ext. $CFCl_3$) resonances at 207·9; (1F, m) and 221·4 (1F, m) (tertiary F), 148·6 (1F, s) and 153·8 (1F, s) (vinylic F), 125·7 (2F, m), 123·1 (1F, m), 121·7 (1F, m), 118·3 and 98·9 (2F, ABq, J_{AB} 244 Hz), and 78·2 (1F, d, *J* 25 Hz) and 85·3 p.p.m. (1F, dd, *J* 25 and 21 Hz) (CH=CF$_2$); the ^1H n.m.r. spectrum showed an asymmetric poorly resolved multiplet centred at 4·0 p.p.m.; (c) 3,3,4,4,7,7,8,8-*octafluorotricyclo*[3,3,0,0^{2,6}]-*octane* (4) (0·17 g, 0·67 mmol, *ca.* 5%) [Found: C, 38·4; H, 1·5%; *M* (mass spectrometry), 252. $C_8H_4F_8$ requires C, 38·1; H, 1·6; *M*, 252], a white solid, ^{19}F n.m.r. 119·6 p.p.m. (sharp s), ^1H n.m.r. (internal Me_4Si) 3·0 p.p.m. (sharp s); (d) 2H,5H-*dodecafluorotricyclo*[4,2,2,0^{2,5}]*dec*-7-*ene* (1) (0·84 g, 2·4 mmol, *ca.* 18%) [Found: C, 34·1; H, 0·3; F, 65·2%; *M* (mass spectrometry), 350. $C_{10}H_2F_{12}$ requires C, 34·3; H, 0·6; F, 65·1%; *M*, 350], a colourless liquid, b.p. 143°, $\nu_{max.}$ 2975 (tertiary C–H) and 1770 cm^{-1} (CF=CF); longer retained products were isolated in an impure state in trace amounts.

The abundance of the long retained products from this reaction varied with the amount of residual ether in the

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[16] W. J. Feast and W. E. Preston, *Tetrahedron*, in the press.

[17] D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1963, 4828.

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

[19] G. Fuller and J. C. Tatlow, *J. Chem. Soc.*, 1961, 3198.

1*H*,2*H*,tetrafluorocyclobutene used. Mass, i.r., ^{19}F, and ^{1}H n.m.r. spectroscopic examination of the mixtures obtained was consistent with their being mixtures of stereoisomers of 1,2,3,4,5,5,6,6-octafluoro-2-(1-hydroxyethyl)bicyclo[2,2,2]octane (5).

Heating 1*H*,2*H*-tetrafluorocyclobutene contaminated with traces of diethyl ether in the absence of perfluorocyclohexa-1,3-diene gave only 3,3,4,4,7,7,8,8-octafluorotricyclo[3,3,0,0^{2,6}]octane (4).

(d) *With cyclohexene*. By the same procedure as in (a), perfluorocyclohexa-1,3-diene (6) (7·14 g, 31·9 mmol) and cyclohexene (2·69 g, 32·8 mmol) heated at 208° in a 75 ml Pyrex ampoule for 24 h gave: (i) a volatile liquid (0·39 g) shown by analytical gas chromatography to be starting materials; (ii) a solid (8·96 g), which was sublimed (60° and 2×10^{-3} mmHg) yielding 1,8,9,10,11,11,12,12-*octafluorotricyclo*[6,2,2,0^{2,7}]*dodec*-9-*ene* (11) (7·86 g, 25·7 mmol, 81%) [Found: C, 47·3; H, 3·6; F, 49·8%; *M* (mass spectrometry), 306. $C_{12}H_{10}F_8$ requires C, 47·1; H, 3·3; F, 49·6%; *M*, 306], a white solid, m.p. 55—56°, b.p. 215°, $\nu_{max.}$ 2976 and 2890 (tertiary C–H) and 1764 cm^{-1} (CF=CF); (iii) a brown involatile oil (*ca.* 1·0 g).

(e) *With cyclopentene*. By the same procedure as in (a), perfluorocyclohexa-1,3-diene (6) (7·16 g, 31·9 mmol) and cyclopentene (2·14 g, 31·4 mmol) heated at 208° in a 70 ml Pyrex ampoule for 24 h gave: (i) starting materials (0·35 g); (ii) 1,7,8,9,10,10,11,11-*octafluorotricyclo*[5,2,2,0^{2,6}]*undec*-8-*ene* (12) (8·83 g, 30·2 mmol, 96%) [Found: C, 45·5; H, 2·8; F, 52·6%; *M* (mass spectrometry), 292. $C_{11}H_8F_8$ requires C, 45·2; H, 2·8; F, 52·0%; *M*, 292], a colourless liquid, b.p. 193°, $\nu_{max.}$ 2976 and 2890 (tertiary C–H) and 1767 cm^{-1} (CF=CF); (iii) residual brown oil, a trace.

Dehydrofluorination of 2H,6H-*Tetradecafluorotricyclo*[5,2,2,0^{2,6}]*undec*-8-*ene* (7).—A thick-walled glass tube (*ca.* 20 × 3 cm diam.) was fitted with an inlet tube reaching almost to the bottom of the tube through which dry nitrogen was passed; the exit from the tube was connected in series with two glass traps cooled in liquid air. The tube was filled about two-thirds full with potassium hydroxide (Hopkin and Williams Ltd. General Purpose Reagent Pellets) and heated in an oil-bath at 150° for 2 h with nitrogen passing, in order to remove the greater part of the absorbed water from the potassium hydroxide. The temperature of the bath was raised to 180° and the olefin (7) (8·34 g) was introduced dropwise into the nitrogen stream; a vigorous reaction occurred and the volatile product collected in the glass traps. After being dried by vacuum transfer from phosphoric oxide the product (5·14 g) was shown to be essentially *perfluorotricyclo*[5,2,2,0^{2,6}]-*undeca*-2,5,8-*triene* (8), one component by analytical gas chromatography (>95%), the only impurity being a trace of starting material. A sample was purified by chromatography (column A, 90°) for analysis [Found: C, 36·8; F, 63·6%; *M* (mass spectrometry), 360. $C_{11}F_{12}$ requires C, 36·7; F, 63·3%; *M*, 360]; the product was a colourless liquid, b.p. 141°, $\nu_{max.}$ 1765 (CF=CF), 1755, and 1735 cm^{-1} (diene system), $\lambda_{max.}$ 277 nm (ε 2800), ^{19}F n.m.r. (ext. $CFCl_3$) resonances at 216·5 (2F, m, at C-1 and C-7), 152·8 (2F, s, at C-8 and C-9), 143·4 (2F, m, at C-3 and C-5), 139·2 and 132·2 (2F, ABq, J_{AB} 309 Hz, at C-4) and 127·7 and 129·5 p.p.m. (4F, pseudo-ABq, J_{AB} 228 Hz, at C-10 and C-11).

Dehydrofluorination of 2H,7H-*Hexadecafluorotricyclo*[6,2,2,0^{2,7}]*dodec*-9-*ene* (9).—Olefin (9) (4·98 g, 11·06 mmol), potassium hydroxide (5 g), and water (10 g), were heated to 140° and stirred vigorously for 10 min. At this point the mixture was darkening rapidly and was quenched by rapid addition of cold dilute aqueous hydrochloric acid (*ca.* 200 ml). Analytical gas chromatography of the fluorocarbon layer indicated that olefin (9) was the major component. The fluorocarbon was separated, mixed with further potassium hydroxide (3 g) and water (6 g), heated to 150°, and mixed for 10 min. Quenching, as before, followed by vacuum transfer of the fluorocarbon layer from phosphoric oxide, gave a two-component product, separated by gas chromatography (column A) to give: (i) *perfluorotricyclo*[6,2,2,0^{2,7}]*dodeca*-2,6,9-*triene* (10) (1·67 g, 4·07 mmol, 37%) [Found: C, 35·4%; *M* (mass spectroscopy), 410. $C_{12}F_{14}$ requires C, 35·1%; *M*, 410], a colourless liquid, b.p. 159°, $\nu_{max.}$ 1767 cm^{-1} (CF=CF), 1742, and 1703 cm^{-1} (diene system), $\lambda_{max.}$ 259 nm (ε 4500), ^{19}F n.m.r. resonances at 215·9 (2F, m, at C-1 and C-8), 152·4 (2F, s, at C-9 and C-10), 134·3 (2F, m, at C-3 and C-6), and 129·2 (8F, complex asymmetric m, at C-4, -5, -11, and -12).

Attempted Dehydrofluorination of 2H,5H-*Dodecafluorotricyclo*[4,2,2,0^{2,5}]*dec*-7-*ene* (1).—(*a*) By use of the technique successfully applied to compound (7), the olefin (1) (0·235 g) was introduced into molten potassium hydroxide at 180°. A vigorous reaction occurred and the initially colourless potassium hydroxide became yellow-brown. The volatile material which was collected (*ca.* 0·1 g) was shown by gas chromatography and i.r. spectroscopy to be predominantly the olefin (1) together with traces of four other compounds.

(*b*) By use of the method successfully applied to compound (9), the olefin (1) (0·44 g), potassium hydroxide (0·8 g), and water (1 g) were kept at 130° for 8 min. After quenching with dilute aqueous hydrochloric acid, a fluorocarbon fraction (*ca.* 0·2 g) was obtained which was shown by i.r. spectroscopy and analytical gas chromatography to be starting material containing only traces of the same four compounds as formed in (*a*).

(*c*) Repetition of the procedure in (*b*) with olefin (1) (0·90 g), potassium hydroxide (0·70 g), and water (1·5 ml) at 160° for 15 min gave essentially the same product as in (*b*). Reheating at 170° for a further 15 min with additional potassium hydroxide (0·5 g) gave a product mixture identical to that obtained before, however only *ca.* 0·1 g of fluorocarbon was recovered.

(*d*) Olefin (1) (0·44 g) stirred at room temperature with water (1 ml) and potassium hydroxide (0·8 g) for 1 h gave a fluorocarbon fraction shown by analytical gas chromatography and i.r. spectroscopy to be unchanged starting material.

In cases (*b*) and (*c*) reaction did occur on heating: the mixture gradually became homogeneous and darkened to a deep brown-black. In case (*d*) the initially colourless solution slowly became deep red, although there was no evidence of reaction in the isolated product.

Retro-diene Reactions of the Diels–Alder Adducts.—Compound (9) (0·094 g) was heated at 335° for 48 h in a 12 ml Pyrex ampoule sealed under vacuum to give a colourless liquid which was shown by gas chromatography and i.r. spectroscopy to contain compound (9) (*ca.* 96%) and a mixture of perfluorocyclohex-1,3-diene (6) and 1*H*,2*H*-octafluorocyclohexene (*ca.* 4%).

Compound (7) (0·090 g) under the same conditions gave a colourless liquid shown by i.r. spectroscopy and gas chromatography to contain only compound (7). Compound (1) (0·094 g) was similarly unaffected under the same conditions.

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