

## Valence-bond Isomer Chemistry. Part V.<sup>1a</sup> Hexafluorobicyclo[2.2.0]-hexa-2,5-diene and its Derivatives as Dipolarophiles<sup>1b</sup>

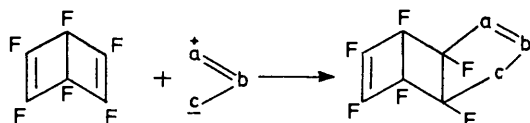
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Hexafluorobicyclo[2.2.0]hexa-2,5-diene is an active dipolarophile, reacting with the representative 1,3-dipoles phenyl azide, diazomethane, 2,2,2-trifluorodiazooethane, 2,4,6-trimethylbenzonitrile oxide, and benzonitrile *N*-phenylimide to give 1 : 1 adducts, and mixtures of 1 : 2 adducts. Related compounds are similarly reactive, addition to the CF:CF double bond of 2-methoxypentafluorobicyclo[2.2.0]hexa-2,5-diene, and of *exo*-5,6-dibromohexafluorobicyclo[2.2.0]hex-2-ene, occurring with phenyl azide and with 2,4,6-trimethylbenzonitrile oxide, respectively. <sup>19</sup>F N.m.r. studies indicate that reaction occurs by *exo*-addition to the bicyclo-compounds.

The phenyl azide adducts, 1,2,3,4,5,6-hexafluoro-9-phenyl-7,8,9-triazatricyclo[4.3.0.0<sup>2,5</sup>]nona-3,7-diene and 1,2,3,5,6,7-hexafluoro-4,10-diphenyl-4,8,9,10-tetra-azatetracyclo[5.3.0.0<sup>2,6</sup>.0<sup>3,5</sup>]dec-8-ene, lose nitrogen upon *u.v.* photolysis in acetone solution, to give the derived aziridines.

HEXAFLUOROBICYCLO[2.2.0]HEXA-2,5-DIENE, readily prepared by the photochemical isomerisation of hexafluorobenzene,<sup>2</sup> is a versatile and reactive compound. The olefinic fluorine atoms may be displaced by a variety of nucleophiles,<sup>3,4</sup> aluminium halides cause replacement of bridgehead fluorine atoms,<sup>3</sup> addition to the double bonds occurs readily,<sup>3,4</sup> and the hexadiene is an active dienophile in the Diels–Alder reaction.<sup>5</sup> In most of its reactions, the bicyclohexane skeleton is preserved, and enhanced reactivity in addition reactions in particular appears to be associated with relief of pronounced angular strain.

Fluoro-olefins are particularly unreactive towards 1,3-dipoles, diazoalkanes failing to react as 1,3-dipoles towards olefins containing vinylic fluorine atoms,<sup>6</sup> and the reactions of organic azides with fluoro-olefins requiring forcing conditions;<sup>7</sup> however cyclo-olefins are particularly reactive, an effect long attributed to the relief of angular strain.<sup>8,9</sup> The strained nature of hexafluorobicyclo[2.2.0]hexa-2,5-diene prompted an investigation



abc = (I) PhN<sub>3</sub>, 42%  
 (II) CH<sub>2</sub>N<sub>2</sub>, 61%  
 (III) 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>:C:N<sup>+</sup>·O<sup>-</sup>, 60%  
 (IV) PhC:N<sup>+</sup>NPh, 10%

of its reactions with a range of 1,3-dipoles, despite the presence of deactivating fluorine substituents. It was found to be an active dipolarophile.

<sup>1</sup> (a) Part IV, M. G. Barlow, J. G. Dingwall, and R. N. Haszeldine, *J.C.S. Perkin I*, 1973, 1542; (b) Preliminary communication, M. G. Barlow, R. N. Haszeldine, and W. D. Morton, *Chem. Comm.*, 1969, 931.

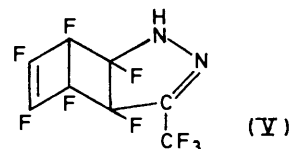
<sup>2</sup> G. Camaggi, F. Gozzo, and G. Cevidalli, *Chem. Comm.*, 1966, 313; I. Haller, *J. Amer. Chem. Soc.*, 1966, 88, 2070.

<sup>3</sup> G. Camaggi and F. Gozzo, *J. Chem. Soc. (C)*, 1969, 489.

<sup>4</sup> M. G. Barlow, R. N. Haszeldine, W. D. Morton, and D. R. Woodward, *J.C.S. Perkin I*, 1972, 2170.

<sup>5</sup> M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc. (C)*, 1971, 90.

Hexafluorobicyclo[2.2.0]hexa-2,5-diene reacted under mild conditions (room temperature or below) with the 1,3-dipoles phenyl azide, diazomethane, 2,4,6-trimethylbenzonitrile oxide, and benzonitrile *N*-phenylimide (prepared *in situ*), to give moderate to good yields of 1 : 1 adducts (I)–(IV), respectively, by *exo*-addition.<sup>4,5</sup> In the case of 2,2,2-trifluorodiazooethane, the tautomeric adduct (V) (75%) was isolated. Formation of 1 : 2



adducts is possible, and this was observed with all but the least reactive, 2,2,2-trifluorodiazooethane.

Addition to the 1 : 1 adduct may occur in two ways and both possible *exo*-adducts were, for the most part, observed. Thus phenyl azide yielded the adduct (VI) (18%) with phenyl groups *trans*-disposed, together with the aziridine (VII) (21%), possibly formed by loss of nitrogen from the unstable adduct (VIII),<sup>10</sup> since the adduct (VI) is stable under the conditions of the experiment, but this was not isolated. An excess of diazomethane gave the adducts (IX) (39%) and (X) (39%), both adducts (XI) and (XII) were apparently formed in equal amounts in the reaction with 2,4,6-trimethylbenzonitrile oxide, and an inseparable mixture (13%) of adducts (XIII) and (XIV) was obtained in the reaction with benzonitrile *N*-phenylimide.

The reactions with 1,3-dipoles are apparently characteristic of the strained cyclobutene portion of the bicyclohexane skeleton. Thus phenyl azide reacted at the

<sup>6</sup> J. H. Atherton and R. Fields, *J. Chem. Soc. (C)*, 1968, 1507; J. P. Tomlinson and R. Fields, personal communication.

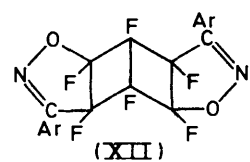
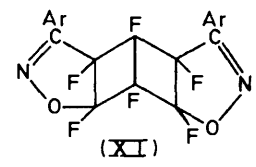
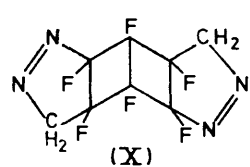
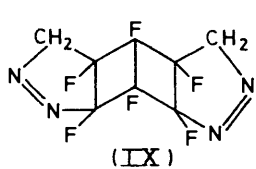
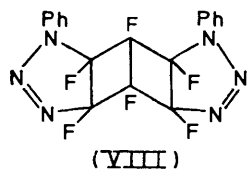
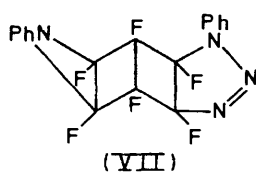
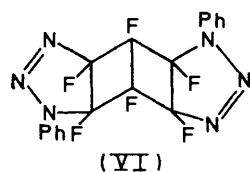
<sup>7</sup> W. Carpenter, A. Haymaker, and D. W. Moore, *J. Org. Chem.*, 1966, 31, 789.

<sup>8</sup> J. H. Boyer and F. C. Canter, *Chem. Rev.*, 1954, 54, 41; 'Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 806.

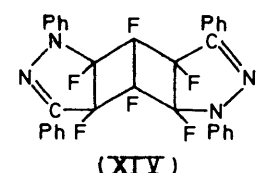
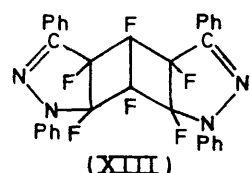
<sup>9</sup> R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, 2, 633.

<sup>10</sup> For a review of triazoline decomposition, see P. Scheiner in 'Selective Organic Transformations,' ed. B. S. Thyagarajan, Wiley-Interscience, New York, 1970, vol. 1, p. 327.

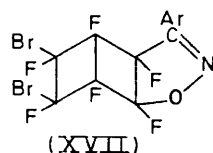
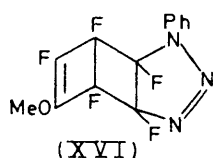
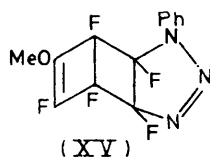
CF:CF double bond of 2-methoxypentafluorobicyclo[2.2.0]hexa-2,5-diene to give an equimolar mixture of the



Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>



adducts (XV) and (XVI), and 2,4,6-trimethylbenzonitrile oxide reacted essentially quantitatively with *exo*-5,6-

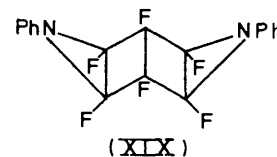
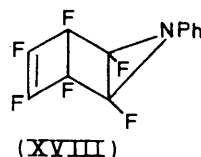


Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>

dibromohexafluorobicyclo[2.2.0]hex-2-ene to give the adduct (XVII). Interestingly, *trans*-5,6-dibromohexa-

fluorobicyclo[2.2.0]hex-2-ene, present during the reaction with the *exo*-dibromide, did not react.

Photolysis, in acetone solution, of the phenyl azide adducts (I) and (VII) yielded the respective aziridines (XVIII) and (XIX).



*Structures of the Adducts.*—For all the 1 : 1 adducts, the FC=CF stretching frequency (1748—1761 cm<sup>-1</sup>) occurred in the range characteristic of such bicyclo[2.2.0]hexene systems.<sup>3-5</sup> In the <sup>19</sup>F n.m.r. spectra (see Table 1) the olefinic fluorine atoms gave rise to absorption bands within the range 40.5—45.1 p.p.m.; this range is characteristic,<sup>4,5</sup> whereas the bridgehead fluorine atom absorptions of the bicyclo[2.2.0]hexene system were rather more variable, occurring in the range 104.0—114.3

TABLE 1

<sup>19</sup>F N.m.r. chemical shifts <sup>a</sup> of hexafluorobicyclo[2.2.0]hexene systems

Compound	$\delta_1^b$	$\delta_2^c$	$\delta_3^e$
(I) <sup>d</sup>	63.6, 66.5	106.1, 114.3	40.5, 42.2
(II) <sup>d</sup>	120.2, 71.7	103.2, 111.3	43.4, 45.1
(III) <sup>e</sup>	82.7, 40.0	104.9, 110.6	40.0, 43.4
(IV) <sup>e</sup>	85.5, 57.5	106.0, 109.0	42.0, 42.0
(V) <sup>f</sup>	88.1, 53.6	104.2, 108.9	42.2, 42.2
(XVIII) <sup>d</sup>	95.4	104.0	43.1
(XV) <sup>g,g</sup>	64.3, 67.3	104.4, 106.9	52.1 <sup>h</sup>
(XVI)	64.3, 67.3	99.0, 111.5	50.5 <sup>h</sup>

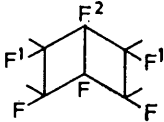
<sup>a</sup> In p.p.m. to high field of external CF<sub>3</sub>·CO<sub>2</sub>H. <sup>b</sup> The first figure refers to the absorption of the CF attached to the atom of lowest atomic weight. <sup>c</sup> Not individually assigned. <sup>d</sup> In Me<sub>2</sub>CO. <sup>e</sup> In CCl<sub>4</sub>. <sup>f</sup> In tetrahydrofuran; CF<sub>3</sub> absorption at -14.0 p.p.m. <sup>g</sup> Containing 50% isomer (XVI); certain assignments to individual isomers are tentative. <sup>h</sup> MeO·C:CF absorption.

p.p.m. In Diels-Alder<sup>5</sup> and other reactions<sup>4</sup> of hexafluorobicyclo[2.2.0]hexa-2,5-diene, we have argued that *exo*-addition is favoured, and is characterised by a deshielding of bridgehead fluorine atoms. In the adducts listed in Table 1, one or both of the bridgehead fluorine atoms (F-2) show variable and fairly substantial deshielding, indicating that *exo*-addition of the 1,3-dipole occurs.

Table 2 shows the chemical shifts of the 1 : 2 adducts, and related compounds. The structure and assignments of individual pairs of adducts, for example (IX) and (X), follow from the number of absorptions, two and one respectively, due to bridgehead fluorine atoms (F-2). These absorptions show substantial deshielding, more

pronounced than in the 1:1 adducts, again indicating *exo*-addition of 1,3-dipole. The bridgehead fluorine atoms of the dibromo-compound (XVII) are particularly deshielded, because of the adjacent *exo*-bromine atoms.<sup>4</sup>

TABLE 2  
<sup>19</sup>F N.m.r. chemical shifts <sup>a</sup> of  
hexafluorobicyclo[2.2.0]hexane systems



Compound	$\delta_1^f$	$\delta_2^g$
(VI) <sup>b</sup>	64.1, 78.1	105.3
(VII) <sup>c</sup>	68.6, 68.6 95.5, 98.2 <sup>h</sup>	100.8, 102.7
(IX) <sup>b</sup>	118.2, 74.8	96.3, 110.8
(X) <sup>b</sup>	107.9, 82.5	99.8
(XI) <sup>b,d</sup>	91.5, 44.5	97.0, 106.5
(XII) <sup>b</sup>	99.8, 54.0	100.6
(XVII) <sup>e</sup>	92.7, 48.2	79.9, 85.0
(XIX) <sup>e</sup>	99.8	93.2

<sup>a</sup> In p.p.m. to high field of external CF<sub>3</sub>·CO<sub>2</sub>H. <sup>b</sup> In tetrahydrofuran. <sup>c</sup> In Me<sub>2</sub>CO. <sup>d</sup> Containing 50% isomer (XII). <sup>e</sup> In CCl<sub>4</sub>; CBr absorption at 38.3 p.p.m. <sup>f</sup> The first figure refers to the absorption of the CF attached to the atom of lowest atomic weight. <sup>g</sup> Not individually assigned.

<sup>h</sup> Absorptions due to CF·CF·NPh.

Also noteworthy are substantial coupling of certain *endo*-fluorine atoms, e.g. in adducts (X) and (XII) splittings ( $J + J'$ ) of 45 and 34 Hz, respectively, are apparent.

Prior to our preliminary communication, only one 1,3-cycloaddition of a *para*-bonded benzene had been reported<sup>11</sup> but recently such additions of bicyclo[2.2.0]hexa-2,5-diene itself,<sup>12</sup> and of its hexamethyl derivative<sup>13</sup> have been described. The ready addition when fluorine is a substituent is remarkable, and presumably reflects relief of ring strain during the addition. The absence of addition to *trans*-5,6-dibromohexafluorobicyclo[2.2.0]hex-2-ene is probably due to the presence of a bulky *endo*-bromine atom; related systems with similar bulky substituents also fail to react.<sup>14</sup>

#### EXPERIMENTAL

Experimental and analytical techniques were similar to those described previously.<sup>4,5</sup>

**Reactions of Hexafluorobicyclo[2.2.0]hexa-2,5-diene with 1,3-Dipoles.**—(a) *With phenyl azide.* (i) *At 34° for 5 days.* The bicyclohexadiene (0.27 g, 1.45 mmol) and phenyl azide<sup>15</sup> (0.44 g, 3.70 mmol) in hexafluorobenzene (0.40 g, 2.15 mmol) were sealed *in vacuo* and kept at 34° for 5 days. Removal of volatile material *in vacuo* gave unchanged hexadiene (0.15 g, 0.81 mmol), phenyl azide (0.10 g, 0.84 mmol), hexafluorobenzene (0.45 g, 2.42 mmol), and a pale yellow residue (0.13

g) which was sublimed at 50° and 0.01 mmHg to give 1,2,3,4,5,6-hexafluoro-9-phenyl-7,8,9-triazatricyclo[4.3.0.0<sup>2,5</sup>]nona-3,7-diene (I) (0.08 g, 0.27 mmol, 42%) (Found: C, 47.4; H, 1.8; N, 13.8. C<sub>12</sub>H<sub>5</sub>F<sub>6</sub>N<sub>3</sub> requires C, 47.2; H, 1.6; N, 13.7%), as a white solid, m.p. 92°, and a residue (0.01 g) shown by i.r. spectroscopy to contain adducts (VI) and (VII) (see later). The 1:1 adduct (I) showed  $\nu_{\max}$ . 3115, 3077, 3049w (C-H str.), 1748s (C=C str.), 1600m (N=N str.), and 1376—1023s cm<sup>-1</sup> (C-F str.).

(ii) *At 34° for 25 days.* The bicyclohexadiene (0.467 g, 2.51 mmol) and phenyl azide (1.043 g, 8.77 mmol) were sealed *in vacuo* and kept at 34° for 25 days. Removal of volatile material *in vacuo* gave nitrogen (0.54 mmol), unchanged hexadiene (0.010 g, 0.05 mmol), hexafluorobenzene (0.156 g, 0.84 mmol), phenyl azide (0.705 g, 5.93 mmol), and a yellow residue (0.615 g), which was sublimed *in vacuo* at 40° to give the 1:1 adduct (I) (0.146 g, 0.48 mmol, 19%), at 70° to give an unidentified yellow-brown solid (0.052 g), and at 80° to give 1,2,3,5,6,7-hexafluoro-4,10-diphenyl-4,8,9,10-tetra-azatetracyclo[5.3.0.0<sup>2,6</sup>.0<sup>3,5</sup>]dec-8-ene (VII) (0.207 g, 0.52 mmol, 21%) (Found: C, 54.4; H, 2.6; N, 14.7. C<sub>18</sub>H<sub>10</sub>F<sub>6</sub>N<sub>4</sub> requires C, 54.3; H, 2.5; N, 14.1%), as a white solid m.p. 128° (decomp.). A residual solid remained which was recrystallised from aqueous acetone to give 1,2,6,7,8,12-hexafluoro-5,11-diphenyl-3,4,5,9,10,11-hexa-azatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>3,12</sup>]dodeca-3,9-diene (VI) (0.190 g, 0.45 mmol, 19%) (Found: C, 50.8; H, 2.3; N, 19.0. C<sub>18</sub>H<sub>10</sub>F<sub>6</sub>N<sub>6</sub> requires C, 50.9; H, 2.4; N, 19.8%), as a white solid, m.p. 118° (decomp.).

The <sup>19</sup>F spectrum of the crude product (27% w/v in acetone), after removal of 1:1 adduct by sublimation, indicated the presence of adducts (VI) and (VII), together with small amounts of impurities (<5%), possibly including adduct (VIII).

The adduct (VII) showed  $\nu_{\max}$ . 3115—2933w (C-H str.), 1597m (N=N str.) and 1389—977s cm<sup>-1</sup> (C-F str.). The adduct (VI) showed  $\nu_{\max}$ . 3115—2924w (C-H str.), 1595m (N=N), and 1366—1015s cm<sup>-1</sup> (C-F str.).

(b) *With diazomethane.* *N*-Methyl-*N*-nitrosotoluene-*p*-sulphonamide (5.1 g, 23.8 mmol) slurried with *n*-decanol (35 ml) was added during 20 min to a stirred solution of sodium (1.0 g) in diethylene glycol (30 ml) contained in a flask evacuated to 0.01 mmHg *via* two traps cooled to -196°. Distillation of the product *in vacuo* through a trap at -78° yielded diazomethane (*ca.* 0.23 g, 5.5 mmol, 23%) contaminated with hydrocarbon impurities (*ca.* 30%). The concentration of diazomethane was estimated before use; the hydrocarbon impurities acted merely as an inert diluent during subsequent reactions of the diazomethane.

(i) *Hexafluorobicyclo[2.2.0]hexa-2,5-diene in excess.* The hexadiene (0.528 g, 2.84 mmol) and diazomethane (*ca.* 0.11 g, 2.64 mmol) in perfluoro-*n*-pentane (5 ml), were warmed from -196 to -45° and shaken in the dark for 30 min to yield nitrogen (1.16 mmol), unchanged hexadiene (0.17 g, 0.91 mmol), perfluoro-*n*-pentane, and 1,2,3,4,5,6-hexafluoro-7,8-diazatricyclo[4.3.0.0<sup>2,5</sup>]nona-3,7-diene (II) (0.27 g, 1.18 mmol, 61%) (Found: C, 37.0; H, 0.7%; M, 228. C<sub>7</sub>H<sub>2</sub>F<sub>6</sub>N<sub>2</sub> requires C, 36.8; H, 0.9%; M, 228), as a white solid, m.p. 95—97°, which was sublimed at 40° and 0.01 mmHg. The residue (0.05 g, 0.18 mmol, 9%) was shown by i.r. spectroscopy to comprise the 1:2 adducts (IX) and (X) (see later).

<sup>11</sup> R. Criegee and F. Zanker, *Chem. Ber.*, 1965, **98**, 3838.

<sup>12</sup> E. E. van Tamelen and D. Carty, *J. Amer. Chem. Soc.*, 1971, **93**, 6102.

<sup>13</sup> L. A. Paquette, R. J. Haluska, M. R. Short, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, 1972, **94**, 529.

<sup>14</sup> M. G. Barlow, G. M. Harrison, R. N. Haszeldine, R. Hubbard, and M. J. Kershaw, unpublished results.

<sup>15</sup> R. O. Lindsey and C. F. H. Allen, *Org. Synth.*, 1955, Coll. Vol. 3, p. 710.

The 1 : 1 adduct (II) showed  $\nu_{\max}$  3003, 2967w, (C-H str.), 1754s (C=C str.), 1550m (N=N str.), and 1370—1026s  $\text{cm}^{-1}$  (C-F str.).

(ii) *With an excess of diazomethane.* The hexadiene (0.56 g, 2.81 mmol) and diazomethane (*ca.* 10 mmol) in hexafluorobenzene (0.78 g, 4.19 mmol) and perfluoro-*n*-pentane (4 ml) were shaken *in vacuo* in the dark at  $-45^\circ$  for 1 h to yield nitrogen (1.0 mmol), a mixture of perfluoro-*n*-pentane and hydrocarbon (7.0 g), unchanged hexadiene (0.18 g, 0.97 mmol), hexafluorobenzene (0.71 g), the 1 : 1 adduct (II) (0.05 g, 0.22 mmol, 12%), and a yellow solid residue, which was sublimed at  $80^\circ$  and 0.01 mmHg to give a white solid (0.39 g). Part of this solid was soluble in acetone and yielded 1,2,6,7,8,12-hexafluoro-3,4,10,11-tetra-azatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>8,12</sup>]dodeca-3,10-diene (IX) (0.185 g, 0.69 mmol, 38%) (Found: C, 35.3; H, 1.6; N, 20.9.  $\text{C}_8\text{H}_4\text{F}_6\text{N}_4$  requires C, 35.5; H, 1.5; N, 20.8%), as a white solid, m.p.  $130^\circ$  (decomp.), and a residue, almost insoluble in acetone, of 1,2,6,7,8,12-hexafluoro-3,4,9,10-tetra-azatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>8,12</sup>]dodeca-3,9-diene (X) (0.185 g, 0.69 mmol, 38%) (Found: C, 35.2; H, 1.5; N, 20.7%), as a white solid, m.p.  $118^\circ$  (decomp.).

The 2 : 1 adduct (IX) showed  $\nu_{\max}$  3012, 2954w (C-H str.), 1558m (N=N str.), and 1410—1214s  $\text{cm}^{-1}$  (C-F str.),  $\tau$  (12% w/v in tetrahydrofuran) 4.24br (m). The 2 : 1 adduct (X) showed  $\nu_{\max}$  3003, 2959w (C-H str.), 1563m (N=N str.), and 1410—1217s  $\text{cm}^{-1}$  (C-F str.),  $\tau$  (3% w/v in tetrahydrofuran) 4.24br (m).

(c) *With 2,4,6-trimethylbenzointrile oxide.* The bicyclohexadiene (0.50 g, 2.7 mmol) and 2,4,6-trimethylbenzointrile oxide<sup>16</sup> (0.35 g, 2.2 mmol) in tetrahydrofuran (20 ml) were sealed *in vacuo* and kept at  $0^\circ$  for 24 h and at room temperature for 3 days. Volatile material was removed *in vacuo* and the residue was chromatographed on alumina, with chloroform elution, to yield 1,2,3,4,5,6-hexafluoro-9-(2,4,6-trimethylphenyl)-7-oxa-8-azatricyclo[4.3.0.0<sup>2,5</sup>]nona-3,8-diene (III) (0.45 g, 1.2 mmol, 60%) (Found: C, 55.7; H, 3.5; F, 32.5; N, 4.3%; *M*, 347.  $\text{C}_{16}\text{H}_{11}\text{F}_6\text{N}_2\text{O}$  requires C, 55.4; H, 3.2; F, 32.8; N, 4.0%; *M*, 347), as a white solid, m.p.  $41-43^\circ$ , and material (0.2 g) tentatively identified by n.m.r. spectroscopy (2.5% w/v in tetrahydrofuran) as an approximately equimolar mixture of 1,2,6,7,8,12-hexafluoro-3,11-bis-(2,4,6-trimethylphenyl)-5,9-dioxa-4,10-diazatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>8,12</sup>]dodeca-3,10-diene and 1,2,6,7,8,12-hexafluoro-3,9-bis(2,4,6-trimethylphenyl)-5,11-dioxa-4,10-diazatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>8,12</sup>]dodeca-3,9-diene,  $\tau$  3.1 (CH) and 8.8 ( $\text{CH}_3$ ),  $^{19}\text{F}$   $\delta$  44.5, 54.0, 91.5, 99.8, and 100.6 (all 2F), and 97.0 and 106.5 p.p.m. (both 1F).

The 1 : 1 adduct showed  $\nu_{\max}$  1755  $\text{cm}^{-1}$  (CF:CF str.),  $\lambda_{\max}$  (hexane) 206—206.5 ( $\epsilon$  14,850), 215—216 (13,600), and 250.5—254 nm (1865).

(d) *With benzonitrile N-phenylimide.* Triethylamine (0.27 g, 2.7 mmol) was added to a solution of *N*<sup>1</sup>-( $\alpha$ -chlorobenzylidene)-*N*<sup>2</sup>-phenylhydrazine<sup>17</sup> (0.50 g, 2.2 mmol) and the bicyclohexadiene (0.50 g, 2.7 mmol) in benzene (20 ml). After 7 days at room temperature, triethylammonium chloride (0.15 g, 1.6 mmol) was filtered from the mixture, volatile material was removed *in vacuo*, and the residue (0.4 g) was chromatographed on alumina (carbon tetrachloride-benzene as eluant). The solvent was removed and the combined residues were sublimed ( $90^\circ$  and 0.1 mmHg) to yield 1,2,3,4,5,6-hexafluoro-7,9-diphenyl-7,8-diazatricyclo[4.3.0.0<sup>2,5</sup>]nona-3,8-diene (IV) (0.10 g, 0.3 mmol, 10%)

(Found: C, 59.8; H, 2.6; F, 29.6; N, 7.1%; *M*, 380.  $\text{C}_{19}\text{H}_{10}\text{F}_6\text{N}_2$  requires C, 60.0; H, 2.6; F, 30.0; N, 7.3%; *M*, 380), as a white solid, m.p.  $100-102^\circ$ , and a residue, which was recrystallised from aqueous acetone to give a mixture of 1,2,6,7,8,12-hexafluoro-3,5,9,11-tetraphenyl-4,5,9,10-tetra-azatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>8,12</sup>]dodeca-3,10-diene and the corresponding 4,5,10,11-tetra-azatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>8,12</sup>]dodeca-3,9-diene (0.20 g, 0.3 mmol, 13%) (Found: C, 67.1; H, 3.5; F, 19.5; N, 9.9%; *M*, 574. Calc. for  $\text{C}_{33}\text{H}_{20}\text{F}_6\text{N}_4$ : C, 66.9; H, 3.5; F, 19.8; N, 9.7%; *M*, 574), m.p.  $208-211^\circ$ .

The 1 : 1 adduct (IV) showed  $\nu_{\max}$  1752  $\text{cm}^{-1}$  (CF:CF str.),  $\lambda_{\max}$  (hexane) 207—208 ( $\epsilon$  12,350), 241—242 (22,600), 279.5 (3900), 288 (3900), and 343—345 nm (15,200).

(e) *With 2,2,2-trifluorodiazethane.* The bicyclohexadiene (0.50 g, 2.7 mmol) and 2,2,2-trifluorodiazethane<sup>18</sup> (0.30 g, 2.7 mmol), sealed *in vacuo* and kept at  $0^\circ$  for 4 h, and at room temperature for 4 weeks, gave 1,2,3,4,5,6-hexafluoro-9-trifluoromethyl-7,8-diazatricyclo[4.3.0.0<sup>2,5</sup>]nona-3,8-diene (V) (0.60 g, 2.0 mmol, 75%) (Found: C, 32.1; H, 0.5%; *M*, 296.  $\text{C}_8\text{HF}_9\text{N}_2$  requires C, 32.4; H, 0.3%; *M*, 296) as a white solid, m.p.  $73-75^\circ$ ,  $\nu_{\max}$  3430s, 3385s (N-H str.), 1758s (C=C str.), and 1611s  $\text{cm}^{-1}$  (N-H def.),  $\lambda_{\max}$  (hexane) 203—203.5 ( $\epsilon$  1780) and 247—248.5 nm (3440).

*Reaction of 2-Methoxypentafluorobicyclo[2.2.0]hexa-2,5-diene with Phenyl Azide.*—2-Methoxypentafluorobicyclo[2.2.0]hexa-2,5-diene<sup>4</sup> (0.50 g, 2.5 mmol) and phenyl azide (0.25 g, 1.5 mmol), sealed *in vacuo* and kept at room temperature for 7 weeks, gave, after removal of material volatile at room temperature, a mixture (n.m.r.: see Table 1) of 1,2,4,5,6-pentafluoro-3-methoxy- and 1,2,3,5,6-pentafluoro-4-methoxy-9-phenyl-7,8,9-triazatricyclo[4.3.0.0<sup>2,5</sup>]nona-3,7-diene (0.40 g, 1.1 mmol, 43%) (Found: C, 49.4; H, 2.7%; *M*, 367. Calc. for  $\text{C}_{13}\text{H}_6\text{F}_5\text{N}_3\text{O}$ : C, 49.2; H, 2.5%; *M*, 367), as a white solid, m.p.  $58-62^\circ$ ,  $\nu_{\max}$  1725 and 1720  $\text{cm}^{-1}$  (CF:C:OMe str.).

*Reaction of 2,4,6-Trimethylbenzointrile Oxide with 5,6-Dibromohexafluorobicyclo[2.2.0]hex-2-ene.*—5,6-Dibromohexafluorobicyclo[2.2.0]hex-2-ene<sup>4</sup> (0.50 g, 1.4 mmol, a 70 : 30 mixture of *cis,exo*- and *trans*-isomers) and 2,4,6-trimethylbenzointrile oxide (0.23 g, 1.4 mmol) in benzene (20 ml) sealed *in vacuo* and kept at room temperature for 3 weeks, gave, after removal of material volatile at room temperature, a residue, which was chromatographed on alumina ( $\text{CCl}_4$  eluant) to give *exo*-3,4-dibromo-1,2,3,4,5,6-hexafluoro-9-(2,4,6-trimethylphenyl)-7-oxa-8-azatricyclo[4.3.0.0<sup>2,5</sup>]non-8-ene (XVII) (0.50 g, 1.0 mmol, 69%) (Found: C, 37.7; H, 2.4; N, 2.9%; *M*, 505.  $\text{C}_{16}\text{H}_{11}\text{Br}_2\text{F}_6\text{NO}$  requires C, 37.9; H, 2.2; N, 2.8%; *M*, 505), as a white solid, m.p.  $112-114^\circ$ , which sublimed at  $100^\circ$  and 0.1 mmHg.

*Photolysis of Phenyl Azide Adducts.*—(a) 1 : 1 Adduct (I). The adduct (I) (0.117 g, 0.38 mmol) and acetone (2.35 g), sealed *in vacuo* in a 5 ml silica tube, were irradiated with u.v. light (Hanovia U.V.S. 500 at 30 cm) for 18 h. Removal of volatile material *in vacuo* gave nitrogen (0.44 mmol), acetone, and 1,2,4,5,6,7-hexafluoro-3-phenyl-3-azatricyclo[3.2.0.0<sup>2,4</sup>]hept-6-ene (XVIII) (0.059 g, 0.21 mmol, 56%) (Found: C, 52.7; N, 4.9%; *M*, 277.  $\text{C}_{12}\text{H}_5\text{F}_6\text{N}$  requires C, 52.0; N, 5.1%; *M*, 277), as a white solid, m.p.  $82-83^\circ$ ,  $\nu_{\max}$  3085—3010w (C-H str.), 1761s (C=C str.), and 1356—1018s  $\text{cm}^{-1}$  (C-F str.). A trace of brown gum remained.

(b) 1 : 2 Adduct (VII). The adduct (VII) (0.064 g, 0.15

<sup>16</sup> C. Grundmann and R. Richter, *J. Org. Chem.*, 1968, **33**, 476.

<sup>17</sup> H. V. Pechman and L. Seeberger, *Ber.*, 1894, **27**, 2121.

<sup>18</sup> H. Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 1458.

mmol) and acetone (1.95 g), sealed *in vacuo* in a 5 ml silica tube, were irradiated with u.v. light for 24 h. Removal of volatile material *in vacuo* gave nitrogen (0.18 mmol), acetone, and a yellow solid residue (0.049 g), which was sublimed at 70° and 0.01 mmHg to give 1,2,4,5,6,8-hexafluoro-3,7-diphenyl-3,7-diazatetracyclo[3.3.0.0<sup>2,4</sup>.0<sup>6,8</sup>]octane (XIX) (0.041 g, 0.11 mmol, 73%) (Found: C, 60.7; H, 2.4;

N, 7.6%; *M*, 368. C<sub>18</sub>H<sub>10</sub>F<sub>6</sub>N<sub>2</sub> requires C, 58.7; H, 2.7; N, 7.6%; *M*, 368), as a white solid, m.p. 119—124°,  $\nu_{\max}$ . 3095—3018w (C-H str.) and 1376—1017m-s cm<sup>-1</sup> (C-F str.).

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