

Valence-bond Isomer Chemistry. Part VIII.¹ Cycloaddition Reactions of Derivatives of Hexafluorobicyclo[2.2.0]hexa-2,5-diene, and of Hexakis(trifluoromethyl)benzvalene

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Certain polyfluorobicyclo[2.2.0]hexa-2,5-dienes and related bicyclo[2.2.0]hex-2-enes are active dienophiles in the Diels–Alder reaction, and 1,3-dipolarophiles, at ambient temperatures. Furan reacts with perfluoro-1,2- and -1,3-dimethyl- and 1,2,5- and 1,3,5-trimethyl-bicyclo[2.2.0]hexa-2,5-dienes, 2*H*-, 2-methyl-, and 2-methoxy-pentafluorobicyclo[2.2.0]hexa-2,5-dienes, and *exo*-5*H*,*exo*-6*H*-, *exo*-5,*exo*-6- and *exo*-5,*endo*-6-dichloro-, and *exo*-5,*exo*-6-dibromo-hexafluorobicyclo[2.2.0]hex-2-enes, to form 1 : 1 adducts; the last compound also forms adducts with cyclopenta-1,3-diene and with buta-1,3-diene. 2*H*-Pentafluorobicyclo[2.2.0]hexa-2,5-diene forms a 2 : 1 adduct also. The apparent order of reactivity of the various double bonds is $\text{CF}:\text{C}:\text{CF}_3 \gg \text{CF}:\text{CF} > \text{CH}:\text{CF} \gg \text{CF}:\text{C}:\text{CH}_3, \text{CF}:\text{C}:\text{OCH}_3$.

Phenyl azide forms 1 : 1 adducts with perfluoro-1,3-dimethyl- and -1,3,5-trimethyl-bicyclo[2.2.0]hexa-2,5-dienes, by addition to the $\text{CF}:\text{C}:\text{CF}_3$ double bonds, and 2,4,6-trimethylbenzoxonitrile oxide forms adducts with the 5,6-dichloro- and *exo*-5*H*,*exo*-6*H*-hexafluorobicyclo[2.2.0]hex-2-enes.

Hexakis(trifluoromethyl)tricyclo[3.1.0.0^{2,6}]hex-3-ene very readily forms adducts with cyclopenta-1,3-diene, pyrrole, and phenyl azide, whereas hexakis(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene is unreactive.

The variation in reactivity is ascribed to the release of various amounts of ring-strain during reaction, modified by the intervention of steric factors. Crowded *endo*-fluorine atoms have large 4J values (28–52 Hz).

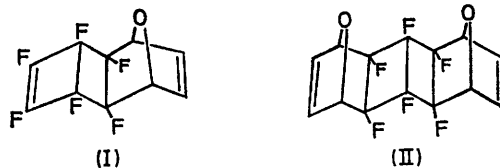
HEXAFLUOROBICYCLO[2.2.0]HEXA-2,5-DIENE is an active dienophile in the Diels–Alder reaction, forming 1 : 1 and 1 : 2 adducts with a variety of acyclic and cyclic dienes,² and a dipolarophile in reactions with 1,3-dipoles, again forming both 1 : 1 and 1 : 2 adducts.³ This reactivity appears to be associated with the strained nature of the bicyclohexadiene, since olefins with fluoro-substituents are normally comparatively unreactive in such cycloadditions. We have investigated this further by examining the reactivity of a number of related polyfluorobicyclo[2.2.0]hexa-2,5-dienes and hex-2-enes.

As a representative diene, we have employed furan,

¹ Part VII, M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, preceding paper.

² M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc. (C)*, 1971, 90.

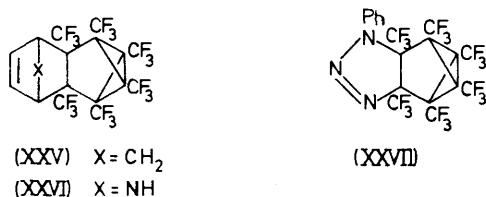
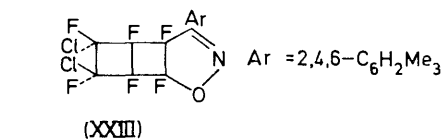
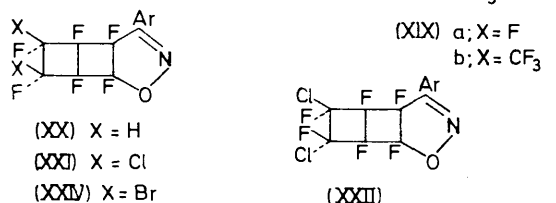
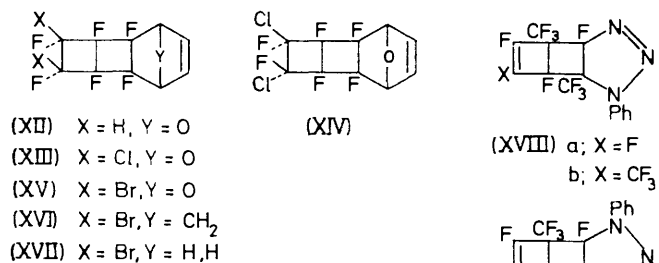
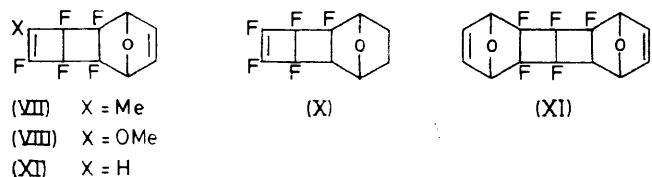
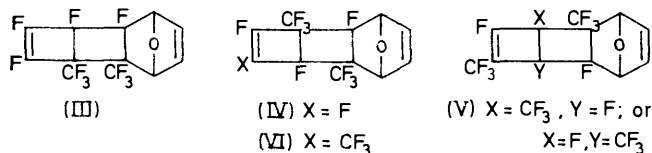
since it readily forms adducts [(I) and (II)] with hexafluorobicyclo[2.2.0]hexa-2,5-diene under mild conditions.²



Furan readily formed monoadducts with perfluoro-1,2- and -1,3-dimethyl- and -1,2,5- and -1,3,5-trimethyl-bicyclo[2.2.0]hexa-2,5-dienes to give adducts (III)–(VI), respectively, by addition to a $\text{CF}:\text{C}:\text{CF}_3$ double bond,

³ M. G. Barlow, R. N. Haszeldine, W. D. Morton, and D. R. Woodward, *J.C.S. Perkin I*, 1973, 1798.

with 2-methyl- and 2-methoxy-pentafluorobicyclo[2.2.0]hexa-2,5-diene to give adducts (VII) and (VIII) by addition to the CF:CF bond, and with 2*H*-pentafluorobicyclo[2.2.0]hexa-2-5-diene to give adducts (IX) and (X),



addition to the CF:CF bond being somewhat favoured. Only with the last hexadiene was a 2:1 adduct (XI) formed. Related bicyclohexenes were similarly active, *exo*-5*H*,*exo*-6*H*-, *exo*-5,*exo*-6- and *exo*-5,*endo*-6-dichloro-, and *exo*-5,*exo*-6-dibromo-hexafluorobicyclo[2.2.0]hexa-2-5-enes readily forming adducts (XII)—(XV), respectively, in high yield, but the *exo*-5,*endo*-6-dibromo-hexene was

much less reactive. The *exo*-5,*exo*-6-dibromide formed analogous adducts (XVI) and (XVII), with cyclopentadiene, and with buta-1,3-diene.

The addition of phenyl azide has long been used as a diagnosis for strained double bonds;⁴ indeed, addition slowly occurred with perfluoro-1,3-dimethyl- and -1,3,5-trimethyl-bicyclo[2.2.0]hexa-2,5-diene to give adducts of structure (XVIII) or (XIX). The rather more active 2,4,6-trimethylbenzonitrile oxide reacted with *exo*-5*H*,*exo*-6*H*-hexafluorobicyclo[2.2.0]hex-2-ene to give the adduct (XX), and with a mixture of 5,6-dichlorohexafluorobicyclo[2.2.0]hex-2-enes to give *cis*-adduct (XXI) and *trans*-adducts (XXII) and (XXIII). We have previously described its reaction with *exo*-5,*exo*-6-dibromohexafluorobicyclo[2.2.0]hex-2-enes, to give the adduct (XXIV).³

Hexakis(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene, the *para*-bonded isomer of hexakis(trifluoromethyl)benzene,⁵ was much less reactive in cycloaddition, failing to react with either cyclopentadiene or phenyl azide, but the benzvalene isomer, hexakis(trifluoromethyl)tricyclo[3.1.0.0^{2,6}]hex-3-ene,⁵ was extremely reactive, reacting very rapidly with cyclopentadiene at room temperature to give the adduct (XXV), rather less readily with the reluctant diene, pyrrole, to give the adduct (XXVI), apparently the second known example of such an addition,² and with phenyl azide to give the adduct (XXVII).

Structures of the Adducts.—For the bicyclohexadienes with two types of double bond, the mode of addition follows readily from the observed C=C stretching frequencies, and from ¹⁹F n.m.r. chemical shifts of olefinic fluorines for the adducts, which are little different from the corresponding values for the parent hexadienes.

We have argued that for hexafluorobicyclo[2.2.0]hexa-2,5-diene cycloaddition occurs by *exo*-addition of the diene or 1,3-dipole,^{2,3} largely on the basis of observed trends of ¹⁹F n.m.r. chemical shifts, particularly those associated with the bridgehead fluorines of the bicyclo[2.2.0]hexane fragment, which often show pronounced deshielding due to adjacent *exo*-substituents. We have also noted that rather large (*ca.* 40 Hz) coupling (⁴*J*) may occur between proximate *endo*-fluorines.^{3,6}

Shown in Tables 1—3 are the ¹⁹F n.m.r. spectral data for the diene and 2,4,6-trimethylbenzonitrile oxide adducts. Certain of the chemical shift assignments are tentative, and are based upon previously noted trends for the hexafluorobicyclo[2.2.0]hexa-2,5-diene adducts and the effects of adjacent substituents. In Table 1, the observed shifts of bridgehead fluorines (F-2 and -5) are consistent with *exo*-addition of the diene,² as are the corresponding shifts in Table 2. In addition, the adduct (XV) may be readily debrominated to the adduct (I). For the adducts of Table 2 with *exo*-substituents, a large splitting corresponding to a $|^4J_{1,3} + ^5J_{1,4}|$ value of 40—51 Hz was apparent. We believe this to be largely

⁴ J. H. Boyer and F. C. Canter, *Chem. Rev.*, 1964, **54**, 41; 'Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 806; R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 633.

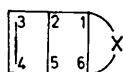
⁵ M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc. (C)*, 1970, 1232.

⁶ M. G. Barlow, R. N. Haszeldine, W. D. Morton, and D. R. Woodward, *J.C.S. Perkin I*, 1972, 2170.

due to substantial four-bond coupling of *endo*-fluorines; support for this was provided by a near-complete analysis

TABLE 1

¹⁹F N.m.r. chemical shifts of bicyclo[2.2.0]hexa-2,5-diene Diels-Alder adducts ^a

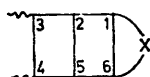


Compound	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
(I) ^b	104.2	115.8	44.4	44.4	115.8	104.2
(III) ^c	97.1	111.9	47.9	41.1	(-15.7)	(-15.7)
(IV) ^d	102.8	(-14.2)	49.5	41.1	113.0	(-14.2)
(V) ^d	96.0	109.1	(-15.8)	1.7	(-15.5)	(-15.5)
(VI) ^c	102.9	(-15.0)	10.2	(-15.8)	110.0	(-15.0)
(VII) ^e	103.0	108.3		27.1	115.4	104.0
(VIII) ^e	105.5	111.0		55.5	115.8	106.3
(IX) ^f	104.1	111.0		15.4	113.8	105.0
(X) ^f	99.9	118.1	45.8	48.0	109.0	

^a Relative to external $\text{CF}_3\cdot\text{CO}_2\text{H}$; values in parentheses correspond to CF_3 groups. ^b From ref. 2. ^c In CFCl_3 . ^d Neat liquid. ^e In CCl_4 . ^f 2:1 Mixture of (IX) and (X) in Me_2CO .

TABLE 2

¹⁹F N.m.r. chemical shifts of bicyclo[2.2.0]hex-2-ene Diels-Alder adducts ^a

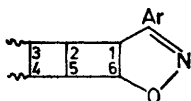


Compound	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
(II) ^b	109.6	111.6	109.6	109.6	111.6	109.6
(XI) ^c	102.9	115.8	107.0	104.8	107.9	
(XII) ^d	110.6	99.0	135.7	135.7	99.0	110.6
(XIII) ^{e,f}	108.7	97.7	40.6	40.6	97.7	108.7
(XIV) ^{e,g}	108.0	96.5	35.0	30.8	109.1	111.1
(XV) ^h	109.0	87.5	37.3	37.3	87.5	109.0
(XVI) ^h	103.0	83.3	36.3	36.3	83.3	103.0
(XVII) ^f	90.3	83.5	37.3	37.3	83.5	90.3

^a Relative to external $\text{CF}_3\cdot\text{CO}_2\text{H}$. ^b From ref. 2. ^c In CDCl_3 . ^d In Me_2CO , $|J_{1,3} + J_{1,4}|$ ca. 40 Hz. ^e 1:1 Mixture of (XIII) and (XIV) in CDCl_3 . ^f $|J_{1,3} + J_{1,4}|$ ca. 51 Hz. ^g With *exo*-3-Cl, analysis yielded ($|J| \geq 4$ Hz): $J_{1,3}$ 52.4, $J_{1,5}$ 16.6, $J_{2,5}$ 20.7, $J_{2,6}$ 15.3, $J_{3,4}$ 13.3, $J_{4,5}$ 6.5 Hz. ^h In CCl_4 , $|J_{1,3} + J_{1,4}|$ 51 Hz. ⁱ In CCl_4 .

TABLE 3

¹⁹F N.m.r. chemical shifts of 2,4,6-trimethylbenzonitrile oxide adducts ^a



Compound	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
(XX) ^b	99.4	90.9	130.3	134.0	99.8	47.4
(XXI) ^{c,d}	96.5	93.8	42.4	43.0	98.4	50.3
(XXII) ^{e,g}	96.4	93.8	36.2	34.0	108.5	53.0
(XXIII) ^{e,f}	99.8	105.1	32.0	38.5	96.4	48.6
(XXIV) ^g	92.7	79.9	38.3	38.3	85.0	48.2

^a Relative to external $\text{CF}_3\cdot\text{CO}_2\text{H}$. ^b In CCl_4 ; $J_{1,3}$ 33, $J_{4,6}$ 28 Hz. ^c 50:23:27 Mixture of (XXI), (XXII), and (XXIII) in CCl_4 . ^d $J_{1,3}$ 42, $J_{4,6}$ 31.5 Hz. ^e $J_{1,3}$ 43 Hz. ^f $J_{4,6}$ 30 Hz. ^g In CCl_4 .

of the spectrum of the *trans*-dichloro-adduct (XIII), giving $J_{1,3}$, the coupling between *endo*-fluorines, as 52.4 Hz.

The 2,4,6-trimethylbenzonitrile oxide adducts of Table 3 provided further examples of substantial 4J values of *endo*-fluorines (28–42 Hz), the larger values reflecting the more crowded environment.

The studies described here indicate that cycloaddition occurs readily to bicyclo[2.2.0]-hexenes and -hexadienes which are not too sterically hindered. Addition to the perfluoromethylhexadienes occurs somewhat less readily than to hexafluorobicyclo[2.2.0]hexa-2,5-diene, ceasing when six trifluoromethyl groups are present. The C:C bonds apparently follow the reactivity sequence $\text{CF}_3\text{C} \gg \text{CF}_2\text{CF} > \text{CH}_2\text{CF} \gg \text{CF}_2\text{C-CH}_3$, $\text{CF}_2\text{C-OCH}_3$, an order which parallels their electrophilicity. For the bicyclohex-2-enes, bulky *endo*-5,6-substituents hinder addition. Interestingly in this respect, *exo*-5,*endo*-6-dibromohexafluorobicyclo[2.2.0]hex-2-ene is reluctant to undergo addition, whereas the corresponding dichloro-compound is about as active as its *cis,exo*-isomer. It appears that this reactivity is associated with the relief of strain in cycloaddition, and in this respect, the benzvalene isomer, hexakis(trifluoromethyl)tricyclo[3.1.0.0.2⁶]hex-3-ene, is very reactive. Molecular models indicate that approach of reactants is here much less hindered than for its *para*-bonded isomer.

EXPERIMENTAL

Experimental techniques were similar to those described previously.^{2,3} Perfluoro-1,2- and -1,3-dimethyl- and -1,2,5- and -1,3,5-trimethyl-bicyclo[2.2.0]hexa-2,5-dienes were prepared by photochemical isomerization of the respective benzenes,^{1,7} hexakis(trifluoromethyl)-*para*-bonded benzene and -benzvalene isomers by photoisomerization of the parent benzene,⁵ 2*H*-, 2-methyl-, and 2-methoxy-pentafluorobicyclo[2.2.0]hexa-2,5-dienes by nucleophilic substitution on hexafluorobicyclo[2.2.0]hexa-2,5-dienes⁶, 5,6-dichloro- (ca. 50:50 mixture of *cis,exo*- and *trans*-isomers) and 5,6-dibromo- (ca. 70:30 mixture of *cis,exo*- and *trans*-isomers) hexafluorobicyclo[2.2.0]hex-2-enes by halogenation of hexafluorobicyclo[2.2.0]hexa-2,5-diene,⁶ and *exo*-5*H,exo*-6*H*-hexafluorobicyclo[2.2.0]hex-2-ene, in improved yield (77%), by hydrogenation of hexafluorobicyclo[2.2.0]hexa-2,5-diene at -45 °C over Pd-C.⁶

Diels-Alder Reactions of Furan.—(a) *With perfluoro-1,2-dimethylbicyclo[2.2.0]hexa-2,5-diene*. The hexadiene (0.097 g, 0.35 mmol) and furan (0.025 g, 0.36 mmol) in trichlorofluoromethane (0.251 g), sealed in an n.m.r. tube at room temperature for 50 days (87% conversion), gave a volatile mixture, shown by g.l.c. (2 m SE30 at 45 °C) to contain unchanged hexadiene (0.013 g, 0.05 mmol, 13% recovery), furan (0.004 g, 0.06 mmol, 16%), and trichlorofluoromethane, and a residue, twice distilled at 25 °C and 0.1 mmHg to give 2,3,4,5-tetrafluoro-6,7-bis(trifluoromethyl)-11-oxatetracyclo[6.2.1.0.2⁷.0.3⁶]undeca-4,9-diene (0.106 g, 0.30 mmol, 100% based on hexadiene converted) (Found: C, 40.7; H, 1.2; F, 53.7. $\text{C}_{12}\text{H}_4\text{F}_{10}\text{O}$ requires C, 40.7; H, 1.1; F, 53.7%), ν_{max} 1770 vs cm^{-1} (CF=CF str.), as a liquid, b.p. 163–164 °C at 755 mmHg (Siwoloboff).

(b) *With perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene*. The hexadiene (0.840 g, 2.96 mmol) and furan (0.198 g, 2.92 mmol), sealed in a 5 ml Rotaflo-tapped ampoule for

⁷ M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, *J.C.S. Perkin I*, 1974, 1736.

3 months at room temperature, gave traces of starting material and 2,4,5,6-tetrafluoro-3,7-bis(trifluoromethyl)-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene (1.020 g, 2.88 mmol, 98%) (Found: C, 41.0; H, 1.3; F, 53.3. C₁₂H₄F₁₀O requires C, 40.7; H, 1.1; F, 53.7%), ν_{\max} 1778 vs cm⁻¹ (CF=CF str.), as a liquid, b.p. 179—180 °C at 754 mmHg.

(c) With *perfluoro-1,2,5-trimethylbicyclo[2.2.0]hexa-2,5-diene*. The hexadiene (0.346 g, 1.03 mmol) and furan (0.079 g, 1.16 mmol) gave (30 days at room temperature, 97% conversion) either 2,3,5-trifluoro-4,6,7-tris(trifluoromethyl)- or 2,5,6-trifluoro-3,4,7-tris(trifluoromethyl)-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene (0.403 g, 1.00 mmol, 100%) (Found: C, 38.7; H, 1.1; F, 56.3. Calc. for C₁₃H₄F₁₂O: C, 38.7; H, 1.0; F, 56.5%), ν_{\max} 1738 vs cm⁻¹ (CF=C-CF₃ str.), as a liquid, b.p. 176—177 °C at 758 mmHg.

(d) With *perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene*. The hexadiene (0.402 g, 1.20 mmol) and furan (1.169 g, 17.18 mmol) gave (26 days at room temperature) unchanged furan (1.086 g, 16.00 mmol, 93%) and 2,4,6-trifluoro-3,5,7-tris(trifluoromethyl)-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene (0.475 g, 1.17 mmol, 98%) (Found: C, 38.6; H, 1.0. C₁₃H₄F₁₂O requires C, 38.7; H, 1.0%), ν_{\max} 1739s cm⁻¹ (CF=C-CF₃ str.), as a liquid, b.p. 171.5—172.5 °C at 760 mmHg.

(e) With 1,2,3,4,5-pentafluorobicyclo[2.2.0]hexa-2,5-diene. The hexadiene (0.815 g, 4.85 mmol) and furan (0.271 g, 3.98 mmol) in diethyl ether (5.03 g), shaken in a 35 ml Pyrex ampoule at room temperature for 14 h, gave volatile material, shown by g.l.c. (6 m PEGA at 25 °C) to comprise pentafluorohexadiene (0.252 g, 1.50 mmol, 33% recovery) and diethyl ether, and a residue, which was washed with cold diethyl ether (2 × 2 ml) and sublimed to give: (i) at 35—40 °C and 1 mmHg, a mixture, shown by ¹⁹F n.m.r. spectroscopy to comprise 2,3,4,6,7-pentafluoro- (0.421 g, 1.78 mmol, 53% based on hexadiene converted) and 2,3,4,5,6-pentafluoro-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene (0.179 g, 0.76 mmol, 23%) (Found: C, 50.8, H, 2.3%; M, 236. Calc. for C₁₀H₅F₅O: C, 51.0; H, 2.1%; M, 236), ν_{\max} 1745m (CF=CF str.) and 1644s cm⁻¹ (CH=CF str.), as a white solid, m.p. 45—48 °C; and (ii) at 75—80 °C and 1 mmHg, 2,3,4,9,10-pentafluoro-15,16-dioxahexacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{3,10}.0^{4,9}]hexadeca-6,13-diene (0.207 g, 0.68 mmol, 20%) (Found: C, 55.4; H, 3.3. C₁₄H₉F₅O₂ requires C, 55.3; H, 3.0%), as a white solid, m.p. 148.5—149 °C.

(f) With 2-methylpentafluorobicyclo[2.2.0]hexa-2,5-diene. The hexadiene (0.20 g, 1.1 mmol) and furan (0.20 g, 2.9 mmol), in carbon tetrachloride (0.4 ml), gave, after 14 days at room temperature, starting materials and 4-methyl-2,3,5,6,7-pentafluoro-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene (0.15 g, 0.6 mmol, 54%) (Found: C, 53.1; H, 3.1%; M, 250. C₁₁H₇F₅O requires C, 52.8; H, 2.8%; M, 250), ν_{\max} 1708s cm⁻¹ (CF=C-CH₃ str.), as a white solid, m.p. 52—54 °C, which sublimed at 45 °C and 0.1 mmHg.

(g) With 2-methoxypentafluorobicyclo[2.2.0]hexa-2,5-diene. The hexadiene (0.40 g, 2.0 mmol) and furan (0.12 g, 1.8 mmol), in diethyl ether (10 ml), give, after 14 days at room temperature, unchanged hexadiene (0.20 g, 1.0 mmol, 50%), and 4-methoxy-2,3,5,6,7-pentafluoro-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene (0.20 g, 0.7 mmol, 37%) (Found: C, 49.4; H, 2.7; F, 35.4%; M, 266. C₁₁H₇F₅O₂ requires C, 49.6; H, 2.6; F, 35.7%; M, 266), ν_{\max} 1728s cm⁻¹ (CF=C-OCH₃ str.), as a white solid, m.p. 72—74 °C, which sublimed at 50 °C and 0.1 mmHg.

(h) With 5,6-dichlorohexafluorobicyclo[2.2.0]hex-2-ene.

The hexene (1.25 g, 4.8 mmol) and furan (0.38 g, 5.6 mmol) gave, after 4 days at room temperature, unchanged dichlorohexene (0.11 g, 0.4 mmol, 9%) and furan (0.09 g, 1.3 mmol), and a residue, subliming at 25 °C and 0.1 mmHg, shown by ¹⁹F n.m.r. spectroscopy to comprise *ca.* equimolar amounts of *exo*- and *trans*-4,5-dichloro-2,3,4,5,6,7-hexafluoro-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undec-9-ene (1.41 g, 4.3 mmol, 99% yield based upon dichlorohexene converted) (Found: C, 37.0; H, 1.4; F, 35.5. Calc. for C₁₀H₄Cl₂F₆O: C, 36.9; H, 1.2; F, 35.1%), as a white solid, m.p. 79—80 °C.

(j) With 5,6-dibromohexafluorobicyclo[2.2.0]hex-2-ene. The hexene (0.30 g, 0.9 mmol) and furan (0.50 g, 7.3 mmol), in diethyl ether (20 ml), gave, after 48 h at room temperature, unchanged dibromohexene (largely the *trans*-isomer) and furan, and a residue, shown by ¹⁹F n.m.r. spectroscopy to be *exo*-4,5-dibromo-2,3,4,5,6,7-hexafluoro-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undec-9-ene (0.22 g, 0.5 mmol, 60%) (Found: C, 23.9; H, 1.3; Br, 38.9. C₁₀H₄Br₂F₆O requires C, 29.0; H, 1.0; Br, 38.6%), as a white solid, m.p. 94.5—95 °C.

The dibromoundecene, when refluxed in acetone solution for 5 h with zinc dust and zinc chloride, gave 2,3,4,5,6,7-hexafluoro-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene (97%), identified by i.r. spectroscopy and mixed m.p.²

(k) With *exo*-5H,*exo*-6H-hexafluorobicyclo[2.2.0]hex-2-ene. The hexene (0.60 g, 3.2 mmol) and furan (0.35 g, 5.2 mmol) gave, after 4 days at room temperature, 2,3,endo-4,endo-5,6,7-hexafluoro-11-oxatetracyclo[6.2.1.0^{2,7}.0^{3,6}]undec-9-ene (0.79 g, 3.1 mmol, 97%) (Found: C, 47.1; H, 2.4; F, 44.3. C₁₀H₆F₆O requires C, 46.9; H, 2.3; F, 44.5%), as white needles, m.p. 160 °C (from acetone).

Reactions of 5,6-Dibromohexafluorobicyclo[2.2.0]hex-2-ene.—(a) With cyclopenta-1,3-diene. The hexene (1.6 g, 4.6 mmol) and cyclopentadiene (2.0 g, 30 mmol) gave, after 48 h at 0 °C, unchanged dibromocyclohexenes (containing *cis,exo*- and *trans*-isomers in the ratio 11:14 by g.l.c.), cyclopentadiene dimer, and a residue, recrystallized from aqueous methanol, to give *exo*-4,*exo*-5-dibromo-2,3,4,5,6,7-hexafluorotetracyclo[6.2.1.0^{2,7}.0^{3,6}]undec-9-ene (0.9 g, 2.2 mmol, 47%) (Found: C, 32.1; H, 1.3; Br, 38.9; F, 27.4%; M 410. C₁₁H₆Br₂F₆ requires C, 32.1; H, 1.5; Br, 38.9; F, 27.6%; M, 410), as a white solid, m.p. 96—97 °C.

(b) With buta-1,3-diene. The hexene (0.80 g, 2.3 mmol) and buta-1,3-diene (0.50 g, 9.3 mmol) gave, after 5 months at room temperature, unchanged dibromohexene (0.60 g, 1.7 mmol, 75%) and butadiene (0.4 g), and a residue, sublimed at 45 °C and 0.1 mmHg, to give *exo*-3,*exo*-4-dibromo-1,2,3,4,5,6-hexafluorotricyclo[4.4.0.0^{2,5}]dec-8-ene (0.25 g, 0.6 mmol, 27%) (Found: C, 30.2; H, 1.7%; M, 398. C₁₀H₆Br₂F₆ requires C, 30.0; H, 1.5%; M, 398), as a white solid, m.p. 54—56 °C.

Reactions of 1,3-Dipoles: Phenyl Azide.—(a) With *perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene*. The hexadiene (0.714 g, 2.50 mmol) and phenyl azide⁸ (0.273 g, 2.55 mmol) in trichlorofluoromethane (0.903 g), sealed in a Pyrex ampoule (10 ml) at room temperature for 25 days, gave volatile material, shown by i.r. spectroscopy and g.l.c. (2 m SE30 at 25 °C) to comprise unchanged hexadiene (0.515 g, 1.80 mmol, 72%) and trichlorofluoromethane, and a green-black residue. This residue was extracted with diethyl ether, the solvent was removed, and the remainder was sublimed at 20 °C and 0.1 mmHg and recrystallized (with charcoal) from light petroleum (b.p. 30—40 °C) to give

⁸ R. O. Lindsay and C. F. H. Allen, *Org. Synth.*, Coll. Vol. III, 1955, p. 710.

either 2,3,4,6-tetrafluoro-9-phenyl-1,5-bis(trifluoromethyl)-7,8,9-triazatricyclo[4.3.0.0^{2,5}]nona-3,7-diene or 1,3,4,5-tetrafluoro-9-phenyl-2,6-bis(trifluoromethyl)-7,8,9-triazatricyclo[4.3.0.0^{2,5}]nona-3,7-diene (0.230 g, 0.57 mmol, 81% yield based upon hexadiene converted) (Found: C, 41.8; H, 1.2; N, 10.2. Calc. for C₁₄H₅F₁₀N₃: C, 41.5; H, 1.2; N, 10.4%), ν_{\max} 1 771vs (CF=CF str.) and 1 602m cm⁻¹ (N=N str.), as crystals, m.p. 45.4 °C. Phenyl azide (0.176 g, 1.48 mmol, 55% recovery) remained from the sublimation. The adduct showed ¹⁹F bands at -13.1 (CF₃·C), -6.3 (CF₃·C·N), 35.9 and 44.0 (:CF), 68.1 (CF·N), and 107.2 p.p.m. (FC).

(b) *With perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene.* The hexadiene (0.516 g, 1.54 mmol) and phenyl azide (0.181 g, 1.52 mmol), in diethyl ether (0.373 g; the reactants were immiscible in the absence of solvent), were sealed in a Pyrex ampoule (10 ml) at room temperature for 2 months. The volatile material, after removal of diethyl ether, comprised two separate layers of unchanged hexadiene (0.329 g, 0.98 mmol, 64% recovery) and phenyl azide (0.102 g, 0.86 mmol, 56%). The pale-yellow residue was sublimed at 40 °C and 1 mmHg and recrystallized (charcoal) from light petroleum to give either 2,4,6-trifluoro-9-phenyl-1,3,5-tris(trifluoromethyl)-7,8,9-triazatricyclo[4.3.0.0^{2,5}]nona-3,7-diene or 1,3,5-trifluoro-9-phenyl-2,4,6-tris(trifluoromethyl)-7,8,9-triazatricyclo[4.3.0.0^{2,5}]nona-3,7-diene (0.233 g, 0.51 mmol, 91% yield based upon hexadiene converted) (Found: C, 39.8; H, 1.2. Calc. for C₁₅H₅F₁₂N₃: C, 39.6; H, 1.0%), ν_{\max} 1 773vs (CF=C·CF₃ str.) and 1 600m and 1 592m cm⁻¹ (N=N str.), as needles, m.p. 81—81.5 °C, ¹⁹F n.m.r. bands at -16.8 (CF₃·C), -14.2 (CF₃·C), -6.9 (CF₃·C·N), 5.5 (:CF), 69.1 (FC·N), and 104.0 p.p.m. (FC).

Reactions of 1,3-Dipoles: 2,4,6-Trimethylbenzoxynitrile Oxide.—(a) *With 5,6-dichlorohexafluorobicyclo[2.2.0]hex-2-ene.* The hexene (1.60 g, 6.25 mmol) and 2,4,6-trimethylbenzoxynitrile oxide⁹ (0.75 g, 4.65 mmol) in benzene (5 ml) were sealed in a Pyrex ampoule (100 ml) at room temperature for 57 days. Material volatile at room temperature was removed, leaving a white solid, which was shown by ¹⁹F n.m.r. spectroscopy to comprise a 50 : 23 : 27 mixture of the *exo-3,exo-4*-, *exo-3,endo-4*-, and *endo-3,exo-4*-isomers of 3,4-dichloro-1,2,3,4,5,6-hexafluoro-9-(2,4,6-trimethylphenyl)-7-oxa-8-azatricyclo[4.3.0.0^{2,5}]non-8-ene (1.84 g, 4.42 mmol, 94%) (Found: C, 46.1; H, 2.8; F, 26.8. Calc. for C₁₆H₁₁Cl₂F₆NO: C, 45.9; H, 2.6; F, 27.3%), as a white solid, m.p. 81—82 °C, which sublimed at 60 °C and 0.1 mmHg.

(b) *With exo-5H,exo-6H-hexafluorobicyclo[2.2.0]hex-2-ene.* The hexene (0.79 g, 4.2 mmol) and 2,4,6-trimethylbenzoxynitrile oxide (0.68 g, 4.2 mmol) in benzene (3 ml), sealed in a Pyrex ampoule (100 ml) at room temperature for 61 days, gave, after removal of material volatile at room temperature, a white solid residue, recrystallized from ethanol, to give 1,2,endo-3,endo-4,5,6-hexafluoro-9-(2,4,6-trimethylphenyl)-7-oxa-8-azatricyclo[4.3.0.0^{2,5}]non-8-ene (1.44 g, 4.1 mmol,

97%) (Found: C, 55.3; H, 3.6; F, 32.2. C₁₆H₁₃F₆NO requires C, 55.0; H, 3.7; F, 32.7%), m.p. 96—97 °C.

Cycloaddition Reactions of Hexakis(trifluoromethyl)tricyclo[3.1.0.0^{2,6}]hex-3-ene.—(a) *With cyclopenta-1,3-diene.* The hexene (0.074 g, 0.153 mmol) and cyclopentadiene (0.083 g, 1.264 mmol) were sealed in a Pyrex ampoule (10 ml) when the initially immiscible reactants became miscible after ca. 1 min, and produced a white solid after 2 min. Unchanged cyclopentadiene (0.071 g, 1.080 mmol, 85%) was removed at room temperature and the white solid residue was sublimed at 35—50 °C and 0.5 mmHg to give 2,3,4,5,6,7-hexakis(trifluoromethyl)pentacyclo[6.2.1.0^{2,7}.0^{3,5}.0^{4,6}]undec-9-ene (0.084 g, 0.153 mmol, 100%) (Found: C, 37.1; H, 1.2%; M, 552. C₁₇H₆F₁₈ requires C, 37.0; H, 1.1%; M, 552), as a white solid, m.p. 150 °C.

The adduct was recovered unchanged after 24 h at 100 °C. Its ¹⁹F n.m.r. spectrum showed bands at -22.65 (3F), -19.10 (3F), -14.45 (6F), and -13.95 p.p.m. (6F).

(b) *With pyrrole.* The hexene (0.147 g, 0.302 mmol) and pyrrole (0.353 g, 5.25 mmol) in hexafluorobenzene (0.286 g) sealed in a Pyrex ampoule (10 ml), were shaken at room temperature for 21 days; removal of material volatile at room temperature left a white solid which was sublimed at 20—45 °C and 0.5 mmHg to give 2,3,4,5,6,7-hexakis(trifluoromethyl)-11-azapentacyclo[6.2.1.0^{2,7}.0^{3,5}.0^{4,6}]undec-9-ene (0.129 g, 0.233 mmol, 77%) (Found: C, 34.8; H, 1.0; F, 62.1; N, 2.6%; M, 553. C₁₈H₅F₁₈N requires C, 34.7; H, 0.9; F, 61.8; N, 2.5%; M, 553), ν_{\max} 3 367w cm⁻¹ (N-H str.), m.p. 83—85 °C.

The adduct, when heated at 100 °C for 24 h, gave unchanged adduct (2%), benzvalene (98%), and pyrrole (98%). Its ¹⁹F n.m.r. spectrum showed bands at -21.35 (3F), -19.60 (3F), and -15.35 p.p.m. (12F).

(c) *With phenyl azide.* The hexene (0.109 g, 0.224 mmol) and phenyl azide (0.208 g, 1.748 mmol), sealed in a Pyrex ampoule (10 ml), were shaken at room temperature for 28 days. Phenyl azide (0.172 g, 1.445 mmol, 85%) was removed *in vacuo* and the pale brown residue was sublimed at 30—50 °C and 0.5 mmHg to give 1,2,3,4,5,6-hexakis(trifluoromethyl)-9-phenyl-7,8,9-triazatetracyclo[4.3.0.0^{2,4}.0^{3,5}]non-7-ene (0.136 g, 0.224 mmol, 100%) (Found: C, 35.6; H, 1.1; F, 56.1; N, 6.7%; M, 605. C₁₈H₅F₁₈N₃ requires C, 35.7; H, 0.8; F, 56.5; N, 6.9%; M, 605), as a white solid, m.p. 70—71 °C, which showed ¹⁹F n.m.r. bands of equal intensity at -26.55, -23.45, -19.65, -18.20, -15.30, and -12.05 p.p.m.

Attempted Reactions of Hexakis(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene.—The hexadiene was recovered unchanged from attempted reaction with cyclopenta-1,3-diene (at room temperature for 2 months), and with phenyl azide (at room temperature for 2 months).

[4/1888 Received, 16th September, 1974]

⁹ C. Grundmann and R. Richter, *J. Org. Chem.*, 1968, **33**, 476.