

Valence-bond Isomer Chemistry. Part III.¹ Some Addition and Nucleophilic Substitution Reactions of Hexafluorobicyclo[2,2,0]hexa-2,5-diene

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Hexafluorobicyclo[2,2,0]hexa-2,5-diene reacts with chlorine or with bromine in the dark to give a mixture of the corresponding *exo,exo*- and *trans*-5,6-dihalogenohexafluorobicyclo[2,2,0]hex-2-enes; further, photochemical reaction with halogen gives a mixture of all-*exo*- and *exo,exo,exo,endo*-2,3,5,6-tetrahalogenohexafluoro[2,2,0]-hexanes. Catalytic hydrogenation of the diene at -50° gives *exo*-5*H*,6*H*]-hexafluorobicyclo[2,2,0]hex-2-ene. Hydrogen bromide adds photochemically to the diene to give mainly the bicyclohexene arising from *cis,exo*-addition; *cis,exo*-addition of bistrifluoromethyl nitroxide to one or both double bonds of the diene is also favoured. The diene is susceptible to nucleophilic displacement of olefinic fluorine atoms; controlled reaction with the nucleophiles sodium methoxide, dimethylamine, methyl-lithium, and sodium borohydride leads to the formation of the appropriate 2-substituted pentafluorobicyclo[2,2,0]hexa-2,5-diene. With potassium benzenethiolate, only the 2,5-disubstituted derivative is formed. Sodium borohydride gives only the 2,6-dihydro-derivative. The diene reacts slowly with lithium halides in dimethylformamide to give halogenopentafluorobenzenes, and with caesium fluoride in formamide to give mainly *exo*-5*H*-heptafluorobicyclo[2,2,0]hex-2-ene.

The n.m.r. spectra of the derived bicyclo[2,2,0]-hexa-2,5-dienes, -hex-2-enes, and -hexanes have been partially or completely analysed. The ^{19}F chemical shifts are particularly useful in deciding the configuration of these compounds. The hexadienes show certain characteristic ranges of F,F coupling constants, viz. low values of the four-bond coupling of olefinic fluorines (0–1.6 Hz), substantial five-bond coupling of olefinic fluorines (9.2–14.7 Hz), and substantial three-bond coupling of bridgehead fluorines (7–14.5 Hz). In the bicyclohexanes, the cross-ring coupling of *endo*-fluorines is very substantial (ca. 40 and 24 Hz); this possibly arises from a 'through-space contribution'. The C:C stretching frequencies of the hexadienes and hexenes, which more nearly resemble those of polyfluorocyclohexenes than those of polyfluorocyclobutenes, are interpreted in terms of a possible contribution from deformation of a long C–C bond between the 1- and 4-positions.

THE photochemical isomerization of hexafluorobenzene to hexafluorobicyclo[2,2,0]hexa-2,5-diene (I), the *para*-

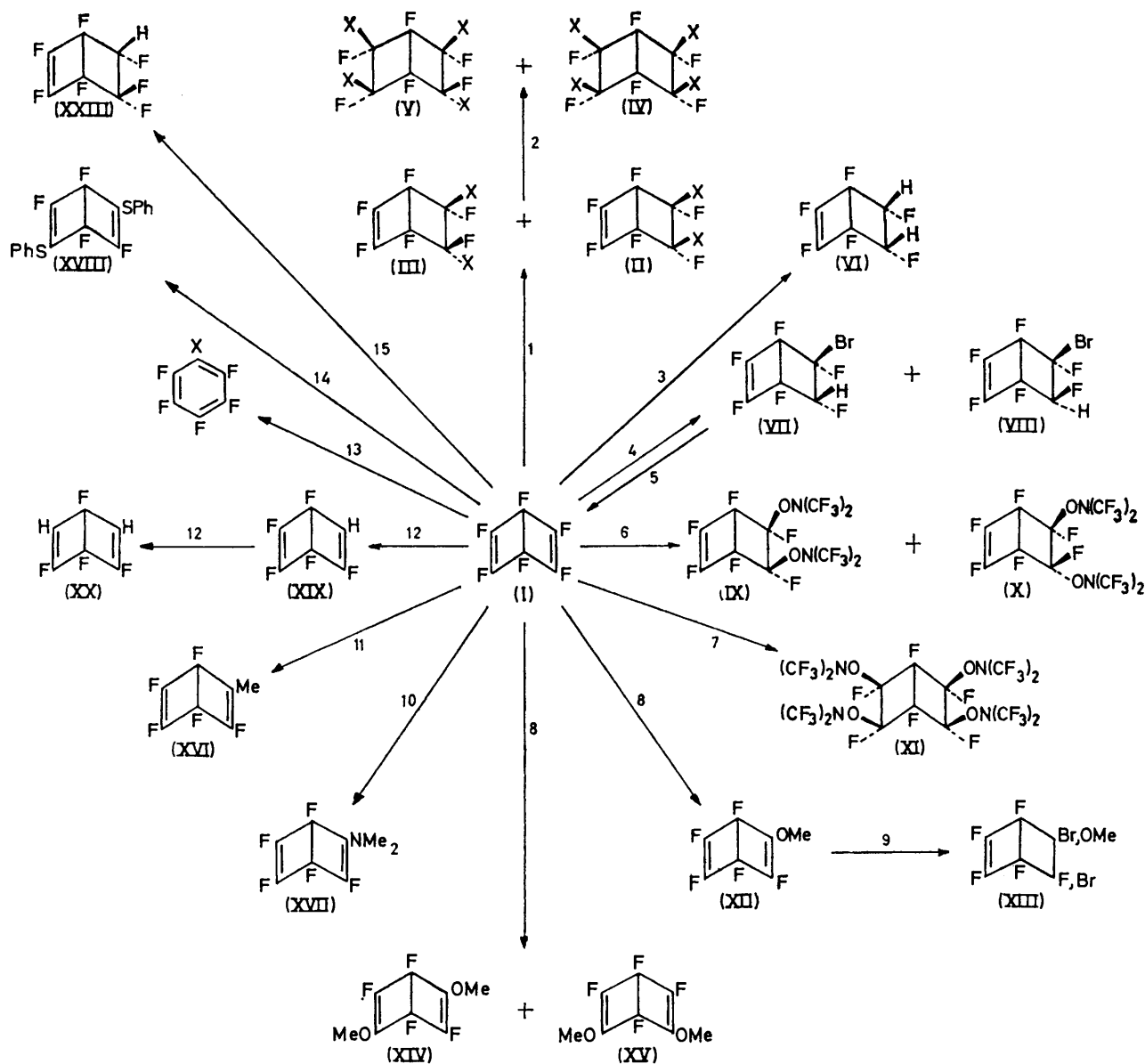
¹ Part II, M. G. Barlow, R. N. Haszeldine, and R. Hubbard *J. Chem. Soc. (C)*, 1971, 90.

bonded valence-bond isomer, was reported independently in 1966 by Camaggi, Gozzo, and Cevidalli,² and by

² G. Camaggi, F. Gozzo, and G. Cevidalli, *Chem. Comm.*, 1966, 313.

Haller,³ and the mechanism of this isomerization has been investigated.⁴ It provides a convenient preparation of this *para*-bonded benzene, and more recently some of its reactions have been described. Camaggi

1-halogeno- and 1,4-dihalogeno-derivatives. The preparation of certain transition-metal derivatives has been reported,⁶ and we have described the reactions of the compound as an active dienophile in the Diels-Alder



SCHEME Reagents: 1, $X_2 = Cl_2$ or Br_2 , dark; 2, $X_2 = Cl_2$ or Br_2 , visible light; 3, H_2 -Pd, -50° , Et_2O ; 4, HBr, u.v. light; 5, solid KOH; 6, $2(CF_3)_2NO\cdot$, 20° , 18 h; 7, $4(CF_3)_2NO\cdot$, 20° , 20 days; 8, NaOMe; 9, Br_2 ; 10, Me_3NH , Et_2O , -23° ; 11, MeLi, Et_2O , -50° ; 12, $NaBH_4$, $(MeO\cdot CH_2\cdot CH_2)_2O$, 0° ; 13, LiX (X = Cl, Br, or I), $Me_2N\cdot CHO$, 20° ; 14, KSPH, Et_2O , 20° ; 15, CsF, $HCO\cdot NH_2$, 50° .

and Gozzo⁵ have described the reactions of hexafluorobicyclo[2,2,0]hexa-2,5-diene with bromine, with hydrogen, with the nucleophiles sodium ethoxide and methyl-lithium to give 2,5- and 2,6-disubstituted products, with sodium borohydride to give 1,2,4-trifluorobicyclo[2,2,0]hexa-2,5-diene, and with aluminium halides to give

reaction,¹ and as a dipolarophile with 1,3-dipoles.⁷ We now describe addition and nucleophilic substitution reactions of hexafluorobicyclo[2,2,0]hexa-2,5-diene which reinforce and extend the work of Camaggi and Gozzo (see Scheme, which summarizes the reactions studied).

⁶ D. J. Cook, M. Green, N. Mayne, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 1771; B. L. Booth, R. N. Haszeldine, and N. I. Tucker, *J. Organometallic Chem.*, 1968, 11, P5.

⁷ M. G. Barlow, R. N. Haszeldine, and W. D. Morton, *Chem. Comm.*, 1969, 931.

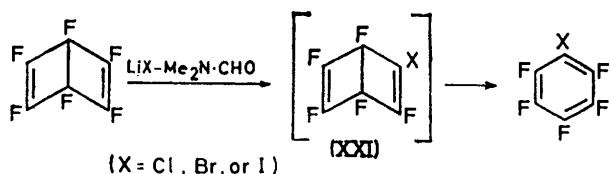
³ I. Haller, *J. Amer. Chem. Soc.*, 1966, 88, 2070.

⁴ I. Haller, *J. Chem. Phys.*, 1967, 47, 1117.

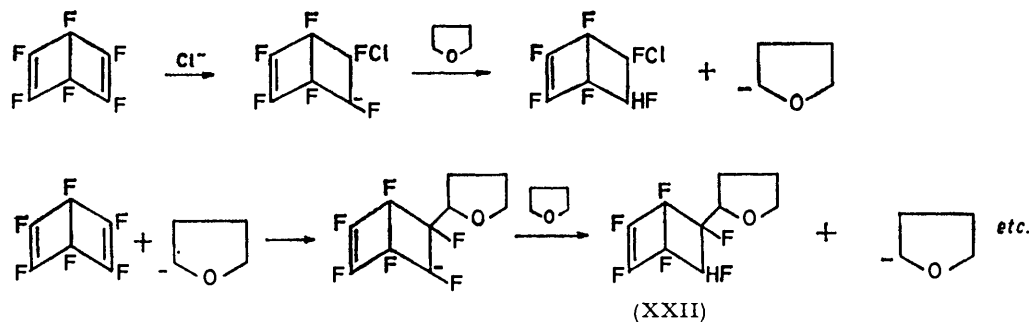
⁵ G. Camaggi and F. Gozzo, *J. Chem. Soc. (C)*, 1969, 489.

The n.m.r. spectra of many of the derived compounds, which were particularly useful in defining their structures, have been partly or completely analysed; these are described and discussed in detail. The i.r. spectra are briefly commented upon.

The hexadiene (I) is susceptible to attack by free radicals. Hydrogen bromide may be added photochemically to give two 5*H*-6-bromohexafluorobicyclo[2,2,0]hex-2-enes (VII) (63%) and (VIII) (27%), where *exo*-addition of a bromine atom occurs, and *exo*-abstraction of a hydrogen atom is favoured. Hydrogen bromide could be readily removed from the hexene (VII) by potassium hydroxide to re-form the diene (I) (67%). The diene (I) reacts with 2 mol. equiv. of bistrifluoromethyl nitroxide to give mainly the *exo*- and *trans*-diadducts (IX) (49%) and (X) (31%), and more slowly with 4 mol. equiv. to give the hexane (XI). In the latter reactions, the hexadiene (I) resembles other fluoro-olefins, including perfluorocyclobutene.⁸ It is, however, more reactive than perfluorocyclobutene, to which hydrogen bromide adds reluctantly.⁹



Controlled reaction of the hexadiene (I) with the moderately active nucleophiles, sodium methoxide,



methyl-lithium, and dimethylamine, produces the corresponding 2-substituted derivative, but with the very active potassium benzenethiolate only the 2,5-disubstituted derivative is formed.

Camaggi and Gozzo⁵ reported that when the bicyclohexadiene (I) was added to an excess of sodium borohydride in bis-(2-methoxyethyl) ether at 0°, 1,2,4-trifluorobicyclo[2,2,0]hexa-2,5-diene was produced (*ca.* 40%), together with 1,2,4-trifluoro- and 1,2,3,5-tetrafluoro-benzene. They suggested that the last compound was produced by isomerization of 1,2,4,6-tetrafluorobicyclo[2,2,0]hexa-2,5-diene (XX). In contrast, we find that the bicyclohexadiene (I) reacts with 0.46 mol. equiv. of sodium borohydride in bis-(2-methoxyethyl)

⁸ R. E. Banks, R. N. Haszeldine, and M. J. Stevenson, *J. Chem. Soc. (C)* 1966, 901.

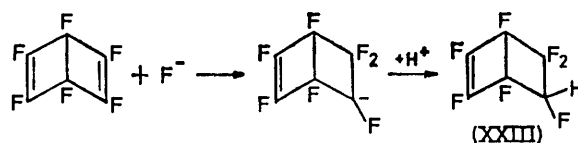
ether at 0° to give 2*H*-pentafluorobicyclo[2,2,0]hexa-2,5-diene (XIX) (80%), and with further sodium borohydride (0.63 mol. equiv.), 1,2,4,6-tetrafluorobicyclo[2,2,0]hexa-2,5-diene (XX) (*ca.* 80%), which isomerizes readily to 1,2,3,5-tetrafluorobenzene at room temperature, is produced and no 1,2,4,5-tetrafluoro-isomer is apparently formed.

A slow reaction of the diene (I) occurred with lithium halide in dimethylformamide at room temperature to produce the corresponding halogenopentafluorobenzene. Presumably reaction proceeds *via* an unstable 2-halogenopentafluorobicyclo[2,2,0]hexa-2,5-diene (XXI), since hexafluorobenzene, which may be produced by slow isomerization of the diene (I), is unaffected by lithium halide under similar conditions. However, compounds of type (XXI) could not be isolated, although there was some spectroscopic evidence (n.m.r.) that the 2-chloro-compound was present in small amounts during the reaction.

With lithium chloride in tetrahydrofuran, the reaction of the bicyclohexadiene (I) took a different course: a compound was isolated which was spectroscopically identified as 5*H*-6-(tetrahydrofuran-2-yl)hexafluorobicyclo[2,2,0]hex-2-ene (XXII) (36%), as a mixture of at least two isomers. It possibly arose by the route shown.

Hexafluorobicyclo[2,2,0]hexa-2,5-diene (I) reacted with caesium fluoride in formamide to give 5*H*-heptafluorobicyclo[2,2,0]hex-2-ene (XXIII) (29%), largely as the *exo*-5*H*-isomer.

¹⁹F N.m.r. Spectra of Bicyclo[2,2,0]-hexa-2,5-dienes, -hex-2-enes and -hexanes: the Structure of Products from



Hexafluorobicyclo[2,2,0]hexa-2,5-diene.—The results described here provide an extension to Cavalli's study¹⁰ and put certain of his tentative conclusions on a firmer basis, but qualify certain others.

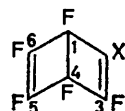
⁹ R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 1956, 61.

¹⁰ L. Cavalli, *J. Chem. Soc. (B)*, 1970, 1616.

Bicyclo[2,2,0]hexa-2,5-dienes. The chemical shifts * of fluorine nuclei in the 2-substituted pentafluorohexadienes are shown in Table 1. Three absorption band systems occur to low field and are assigned to the olefinic fluorines, and two others occur well to high field and are assigned to the bridgehead fluorines, F-1 and F-4. Two of the bands due to olefinic fluorines are little shifted from the absorption band due to olefinic fluorines in the

TABLE 1

¹⁹F Chemical shifts of some 2-substituted pentafluorobicyclo[2,2,0]hexa-2,5-dienes



Substituent	Chemical shift (p.p.m.)				
	δ_1	δ_3	δ_4	δ_5	δ_6
X					
OMe	107.5	56.3	113.8	42.6	44.9
NMe ₂	102.6	68.3	112.5	43.1	49.7
Me	107.6	28.5	114.7	43.7	42.4

parent compound (I) and are assigned to F-5 and F-6 on the unsubstituted double bond. One of the bridgehead fluorine absorptions is well shifted from that of the

assignment of F-5 and F-6. They are assigned on the basis of $|J_{3,5}|$ and $|J_{3,6}|$ (see later).

Compared with the parent compound (I), the absorptions due to olefinic fluorines, F-3, are shifted to high field by the electron-donating OMe and NMe₂ substituents. These observations parallel those reported for 1-substituted pentafluorocyclobutenes, but the extent of the substituent effect is smaller for the cyclobutenes.¹¹ There is a smaller shielding effect, of substituent upon the neighbouring bridgehead F-1, and the remaining fluorine nuclei are little affected, and in no obvious manner.

F-3 (see Table 2) is substantially coupled (13.4—14.7 Hz) to one of the other olefinic fluorines, assigned as F-6, and only weakly coupled (<1 Hz) to the other, assigned as F-5. This is in accord with previous assignments,¹⁰ and supported by examples of substituted bicyclo[2,2,0]hexa-2,5-dienes where the appropriate assignments are unequivocal.^{10,12}

Cavalli¹⁰ has suggested that fluorinated bicyclo[2,2,0]hexa-2,5-dienes have F,F coupling constants characterized by low numerical values for ${}^3J_{5,6}$ (1—4 Hz) and ${}^4J_{3,5}$ (ca. 0 Hz), and high numerical values of ${}^6J_{3,6}$ (13—14 Hz). The values reported for 2-substituted

TABLE 2

F,F Coupling constants for some 2-substituted pentafluorobicyclo[2,2,0]hexa-2,5-dienes

Substituent	Coupling constant (Hz) ^a									
	$J_{1,3}$	$J_{1,4}$	$J_{1,5}$	$J_{1,6}$	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$
H ^b	7.8	7.6	9.7	7.4	4.3	0.8	13.9	7.8	9.6	3.7
OMe ^c	12.2	11.3	10.1	7.7	4.4	≤ 0.3	14.3	7.9	9.5	3.4
NMe ₂ ^d	14.2	14.5	9.9	7.9	1.6	≤ 0.3	14.4	8.3	9.3	3.9
Me ^e	?	?	?	7.6	?	< 1	14.7	8.2	9.3	3.7

^a Magnitudes, unless otherwise stated. ^b Cf. ref. 10, $J_{1,H}$ 3.3, $J_{3,H}$ 10.1, $J_{4,H}$ 2.0, $J_{5,H}$ 3.7 Hz. ^c $J_{1,H}$ 0.5, $J_{3,H}$ 1.7 Hz. ^d $J_{1,H}$ 1.6, $J_{3,H}$ 1.2 Hz. ^e Because of poorly resolved long-range coupling to the protons and lack of spectral intensity, accurate values of the remaining coupling constants could not be obtained.

TABLE 3

N.m.r. parameters of some 2,5- and 2,6-disubstituted tetrafluorobicyclo[2,2,0]hexa-2,5-dienes

Compound	Spin system	Assignment	Chemical shift	Coupling constants (Hz) ^a		
				$J_{1,3}$ 12.8	$J_{1,4}$ 13.6	$J_{3,4}$ 4.8
2,6-(OCH ₃) ₂ ^b	First order	F-1	103.5			
		F-3, F-5	56.5			
		F-4	115.5			
2,6-H ₂ ^c	AA' XX' G M	H-2, H-6	20.8	$(J_{2,3}, J_{5,6}) \pm 10.0$	$(J_{2,6}) 0.0$	$(J_{1,2}, J_{1,6}) 3.5$
		F-3, F-5	107.8	$(J_{2,5}, J_{3,6}) \mp 3.0$	$J_{3,5} 1.6$	$(J_{2,4}, J_{4,6}) 1.9$
		F-1	113.1	$J_{1,3}, J_{1,5} 6.05$	$J_{1,4} 7.05$	$J_{3,4}, J_{4,5} 3.45$
		F-4	101.0	$J_{1,4} 5.2^d$ $J_{3,6} 9.3^d$	$J_{1,6}, J_{3,4} \mp 8.3$ $J_{1,3}, J_{1,5} \pm 9.5$	

^a Moduli unless a sign is given; values in parentheses involve coupling to proton. ^b Parameters are similar to those of the 2,6-diethoxy-compound.¹² ^c Tentative assignment based upon trends of parameters for compounds (I) and (XIX). ^d Tentative assignments.

parent compound (I) and is assigned to F-1, nearest to the varying substituent; in the case of the OMe and NMe₂ substituents, it showed long-range coupling to the side-chain protons. There remains then the individual

* All chemical shifts are given in p.p.m. to high field of external trifluoroacetic acid; where certain compounds in the literature were referenced on the ϕ^* scale, they were brought to an approximately common scale by subtraction of 78 p.p.m.

derivatives in Table 2 bear out this suggestion, but it is more difficult to make generalizations concerning the remaining coupling constants. Those involving the substituted cyclobutene ring portion are particularly variable. Some of the data of Table 3 indicate that

¹¹ R. K. Harris and R. Ditchfield, *Spectrochim. Acta*, 1968, **24A**, 2089.

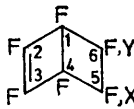
¹² L. Cavalli, *J. Chem. Soc. (B)*, 1967, 384.

these generalizations may need modification for more complex derivatives.

Bicyclo[2,2,0]hex-2-enes. Table 4 shows chemical shift data for the bicyclo[2,2,0]hex-2-enes examined in

TABLE 4

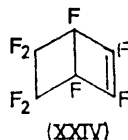
^{19}F Chemical shifts of some 5,6-disubstituted hexafluoro-bicyclo[2,2,0]hex-2-enes



Substituent	Chemical shift (p.p.m.)					
	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
X, Y						
F, F ^a	123.4	42.0	42.0	123.4	52.3	52.3
F, <i>exo</i> -H	107.0	41.6	45.2	120.4	40.4	41.0
<i>exo</i> -H, <i>exo</i> -H	104.2	44.0	44.0	104.2	127.1	127.1
<i>exo</i> -Cl, <i>exo</i> -Cl ^b	107.4	41.3	41.3	107.4	38.6	38.6
<i>endo</i> -Cl, <i>exo</i> -Cl ^b	105.4	40.8	42.5	117.8	40.1	31.2
<i>exo</i> -Br, <i>exo</i> -Br ^c	99.3	41.2	41.2	99.3	37.0	37.0
<i>endo</i> -Br, <i>exo</i> -Br ^c	96.4	40.8	42.4	117.2	31.0	24.6
<i>exo</i> -Br, <i>exo</i> -H	105.2	40.3	43.8	100.0	50.0	111.4
<i>exo</i> -Br, <i>endo</i> -H	123.4	40.7	42.4	93.6	33.6	104.0
<i>exo</i> -ON(CF ₃) ₂ , <i>exo</i> -ON(CF ₃) ₂ ^d	116.2	42.8	42.8	116.2	32.9	32.9
<i>endo</i> -ON(CF ₃) ₂ , <i>exo</i> -ON(CF ₃) ₂ ^e	117.4	40.0	42.2	118.8	48.2	35.4

^a From ref. 14. ^b Mixture of equimolar amounts of isomers. ^c Cf. ref. 10; mixture of isomers in the ratio 70 : 30. ^d CF₃ absorption at -10.0 p.p.m. ^e CF₃ absorptions at -9.7 and -9.3 p.p.m.

this work. Cavalli has also examined the two dibromoderivatives,¹⁰ along with six other 5,6-dibromobicyclo[2,2,0]hex-2-enes, but his results and conclusions differ from ours. In particular, the shifts he reports for the olefinic fluorines, F-2 and F-3, are, allowing for the different conditions used, *ca.* 15 p.p.m. to high field of ours, although we agree closely with his values for the remaining nuclei. We also differ in our respective assignments for F-5 and F-6 (see later).



Common to all the bicyclohexenes are olefinic fluorines, which absorb in the range 40.0–45.2 p.p.m., and bridgehead fluorines, which absorb in the range 93.6–123.4 p.p.m., which are readily assigned, although it is more difficult to assign individual pairs of nuclei within each group. We take as a basis for our structural assignments, the recently reported¹³ octafluorobicyclo[2,2,0]hex-2-ene (XXIV), and consider the effect on the chemical shifts of the remaining fluorines of replacing one or two of the fluorines of the CF₂ groups by a hydrogen, chlorine, or bromine atom. It is expected that the shielding of *cis*-vicinal fluorines, in particular,

¹³ W. J. Feast, W. K. R. Musgrave, and R. G. Weston, *Chem. Comm.*, 1970, 1337.

will be most pronounced if a bromine atom is introduced. These effects will be treated on a purely empirical basis and an internally consistent argument will be looked for, rather than a basis of semi-empirical calculations^{10,14} of doubtful validity, which require assumptions concerning the geometry of these bicyclohexenes, which may be in considerable error.

Compound (XXIV) has its bridgehead fluorine absorption at 123.4 p.p.m., and replacement of an adjacent fluorine by a hydrogen atom causes a low-field shift of 16.4 p.p.m., suggesting that the hydrogen atom is *exo*. The difluoromethylene groups give rise to an AB-type absorption at 41.0 and 52.3 p.p.m. in compound (XXIV) and at 38.0 and 40.4 p.p.m. in the *exo*-6-*H*-compound, implying a low-field shift of at least 11.9 p.p.m. for the fluorine atom giving rise to the 52.3 p.p.m. band in (XXIV). This is therefore assigned to the *exo*-fluorines, and the 41.0 p.p.m. band to the *endo*-fluorines. In the 5*H*,6*H*/-compound the bridgehead fluorine signals are also shifted to low field compared with compound (XXIV); the former is thus the *exo*-5*H*,6*H*/-compound. The presence, or absence, of a low-field shift of bridgehead fluorines completes the identification of the six chlorine- or bromine-containing compounds. In the compounds with *trans*-halogens, F-5 is assigned to the band at highest field of the pair due to halogenofluoromethylene groups, that is, as in compound (XXIV), the high-field band is assigned to *exo*-fluorine. The assignment to *endo*-fluorine (F-6) seems improbable since in the dichlorides it requires that changing from *trans*-chlorine in the *exo*-dichloride to *cis*-chlorine in the *trans*-dichloride causes the *endo*-fluorine absorption to change from 38.6 to 40.1, a high-field shift.

In compounds containing hydrogen the band due to fluoromethylene groups was always readily identified by the presence of the characteristically large (*ca.* 50 Hz) geminal H,F coupling. In the compounds containing ON(CF₃)₂ groups, only a small, but distinct, low-field shift of bridgehead fluorines is observed, but the *trans*-isomer has an absorption at 48.2 p.p.m. (due to F-5) well to high field of that of F-6, and of the corresponding absorption in the *cis*-isomer. It is suggested, therefore, that this band at 48.2 p.p.m. is due to an *exo*-fluorine atom. In these compounds, individual assignment of olefinic fluorines, F-2 and F-3, in compounds showing two types of fluorine, is not unequivocal. Cavalli has tentatively assigned these on the basis of the magnitudes of couplings of bridgehead to olefinic fluorines (³*J* > ⁴*J*), using 1-methoxypentafluorocyclobutene as a model compound. In Table 5 are collected magnitudes of coupling constants for the three bicyclohexenes which we have fully analysed. The spectra of these compounds were complex but first-order. The spectra of the remaining compounds were so complex, or poorly resolved, as to defeat analysis. We have arbitrarily assumed that ³*J*|*J*_{1,2}*J*_{3,4}| > ⁴*J*|*J*_{1,3}*J*_{2,4}| for the couplings

¹⁴ J. Feeney, L. H. Sutcliffe, and S. M. Walker, *Mol. Phys.* 1966, **11**, 117.

within the cyclobutene portion. Some of the remaining compounds in Table 4, which were not analysed, may lack even this consistency. In perfluorocyclobutene,¹¹ 3J and 4J are of the same sign, and have magnitudes of 16.37 and 6.77 Hz, while in 1-methoxypentafluorocyclobutene,¹⁰ if the difluoromethylene groups are correctly assigned, and the long-range coupling of proton to adjacent CF_2 group fluorines supports this, then $^3J = \pm 20.03$ and $^4J = \pm 7.89$ Hz. However, 3- and 4-substituents may have a major effect on these coupling

chlorine, and bromination of an adjacent double bond should not have a major effect upon the geometry of the bridgehead atoms. It is notable in this respect that the *trans*-dibromide from 1-chloropentafluorobicyclo[2,2,0]hexa-2,5-diene has an absorption at ϕ^* 169.3, little different from the one absorption at ϕ^* 172.1 in the *trans*-dibromide from hexafluorobicyclo[2,2,0]hexa-2,5-diene, which has an adjacent *cis*-bromine atom. The corresponding absorptions in the *cis*-dibromides are at ϕ^* 171.0 and 175.1. Thus the assignments (XXIX) and

TABLE 5

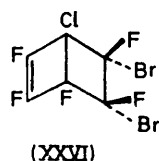
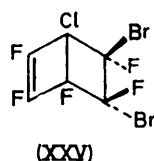
F,F Coupling constants (in Hz) for some 5,6-disubstituted hexafluorobicyclo[2,2,0]hex-2-enes

Substituents	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{1,5}$	$J_{1,6}$	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{2,6}$	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$
<i>endo</i> -Cl, <i>exo</i> -Cl	21.0	7.5	2.3	12.1	2.9	14.3	9.0	2.3	6.8	22.8	1.4	2.6	5.4	9.9	1.5
<i>exo</i> -Br, <i>endo</i> -H ^a	16.0	9.5	2.5	6.5	3.0	11.2	4.5	≤ 0.5	2.5	16.8	2.5	10.5	5.5	5.5	10.8
<i>exo</i> -Br, <i>exo</i> -H ^b	15.7	7.0	≤ 0.3	6.4	8.9	11.3	5.4	≤ 0.5	2.6	15.1	1.8	2.0	11.0	1.5	8.3

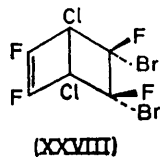
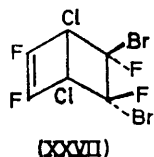
^a $J_{1,H}$ ca. 0.8, $J_{3,H}$ ca. 0.8, $J_{4,H}$ 5.2, $J_{5,H}$ 4.8, $J_{6,H}$ 52.5 Hz. ^b $J_{1,H}$ 6.7, $J_{3,H}$ 1.9, $J_{4,H}$ 1.4, $J_{5,H}$ 1.5, $J_{6,H}$ 51.4 Hz.

constants. For example, in *cis*-3,4-dichlorotetrafluorocyclobutene, 3J and 4J are 11.6 and 4.1 Hz (same sign; not assigned), whereas in the *trans*-isomer they are 10.9 and 1.4 Hz.¹⁵ Apparently 3- and 4-substituents in cyclobutenes may have a substantial effect upon $^3J_{1,2}$ and $^4J_{1,3}$ F,F couplings, so the assignment of olefinic fluorines in the bicyclo[2,2,0]hex-2-enes is left tentative.

Cavalli¹⁰ has assigned the products of bromination of 1-chloropentafluorobicyclo[2,2,0]hex-2,5-diene as the *trans*-dibromide (XXV) and the *endo*-dibromide (XXVI)

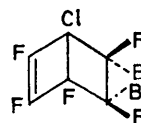


and the products of bromination of 1,4-dichlorotetrafluorobicyclo[2,2,0]hexa-2,5-diene as the *trans*-dibromide (XXVII) and the *endo*-dibromide (XXVIII), largely on the basis of the calculated chemical shift of the bridgehead fluorine in compounds (XXV) and (XXVI) and the long-range F,F coupling constants in compound (XXVIII). We disagree with the assignments for compounds (XXV), (XXVI), and (XXVIII), on the following grounds. The calculated electric-field effects of chlorine and bromine upon the shift of the bridgehead fluorine in compounds (XXV) and (XXVI) probably much

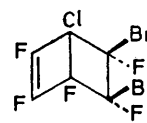


over-estimate the contribution of the chlorine atom. In hexafluorobicyclo[2,2,0]hexa-2,5-diene, the absorption due to bridgehead fluorines occurs at ϕ^* 191.0, while in the 1-chloro-compound the corresponding absorption occurs at ϕ^* 192.8, a marginal high-field effect arising from replacement of adjacent bridgehead fluorine by

(XXX) are indicated. In support of these, the chemical shifts of the CFBr group fluorines may be considered. The data of Table 4 indicate that an *exo*-chlorine at



(XXIX)

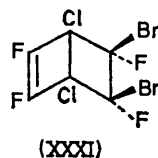


(XXX)

C-5 or C-6 causes a low-field shift of the adjacent bridgehead fluorine of ca. 16 p.p.m., while an *endo*-chlorine or a chlorine a further carbon atom removed has a much smaller effect. If an *exo*-chlorine at C-6 has a similar effect upon a fluorine at C-1 as a chlorine at C-1 upon an *exo*-fluorine at C-6, and our assignment of *trans*-5,6-dibromohexafluorobicyclo[2,2,0]hex-2-ene is accepted, then we predict that compound (XXIX) should show absorptions at ca. ϕ^* 92 and 100 (reported values are 94.0 and 97.0 for the *trans*-dibromide), whereas the *cis*-dibromide (XXX) should show absorptions a little shifted to low field from those of the *exo*-dibromide of the compound (I). The compound assigned structure (XXX) absorbs at ϕ^* 109.4 and 109.8, whereas the *exo*-dibromide from compound (I) absorbs at ϕ^* 113.8. Introduction of a second bridgehead chlorine atom in compounds (XXIX) and (XXX) should have little effect upon the shifts of the CFBr group fluorines. Cavalli¹⁰ reports that the unequivocally *trans*-isomer shows absorptions at ϕ^* 91.8 and 92.8 (a low-field shift of 2–4 p.p.m.), and the *cis*-isomer has ϕ^* 104.0 (low-field shift of 5.5 p.p.m.). The *cis*-dibromide from the 1,4-dichlorohexadiene may therefore be the *exo*-dibromide (XXXI). Cavalli has argued that the absence of apparent long-range spin-spin coupling between distinct fluorines in the latter compound is indicative of *exo*-fluorines. However, the data, in Table 5, for the *exo*-bromo,*exo*-H-compound indicate that this may be true for the coupling of *endo*- to olefinic fluorines.

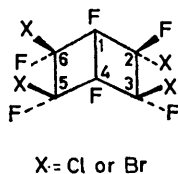
¹⁵ M. G. Barlow, J. M. Brierley, and R. N. Haszeldine, unpublished results.

The magnitudes of the vicinal H,F couplings in the hydrogen-containing bicyclohexenes, where larger values are associated with near eclipsed nuclei, are in accord with the suggested angular dependence of these couplings,¹⁶ and support the proposed configurations and



assignments. There is a marked change in the magnitude of the coupling constant (3J) between olefinic fluorines in going from the bicyclohexadienes, where the range is 3.1—3.9 Hz, to the bicyclohexenes, where a range of 11.2—14.3 Hz is observed.

Bicyclo[2,2,0]hexanes. Present in the product of complete chlorination or bromination of hexafluorobicyclo[2,2,0]hexa-2,5-diene, in addition to the all-*exo*-tetrahalide, were components which showed six types of fluorine, which must therefore be either the *exo,exo,exo,endo*-, or *exo,endo,endo,endo*-isomers. In each case, one bridgehead fluorine had a very similar chemical shift to that of the bridgehead fluorines in the all-*exo*-isomer, and thus probably has two adjacent *exo*-halogens, while the other appeared well to high field of it, having only one adjacent *exo*-halogen. The isomers have therefore *exo,exo,exo,endo*-halogens. The assignment of the four remaining fluorines (CFX) is not certain. However, two fluorines have chemical shifts very similar to those of the CFX absorptions in the corresponding all-*exo*-isomers, while one of the remaining is shifted a little to low field and the other is substantially so shifted. It is expected that F-5 and F-6, which are



in an environment most similar to that of the CFX fluorines in the other isomer, should be least shifted. It is difficult to predict where F-2 should absorb, but F-3 should be shifted to low field (compared with F-5 and F-6) by the adjacent *cis*-halogen. In the dihalogeno-derivatives (see Table 4), a *cis*-halogen causes a low-field shift of 7.4 for chlorine and 12.4 p.p.m. for bromine, when *cis*- and *trans*-isomers are compared. It is difficult, however, to predict what effect the loss of the double bond and the increased crowding of *endo*-substituents should cause. If the bands at lowest field are assigned to F-3, then the apparent low-field shifts are 11.7 and 19.4 p.p.m. for *cis*-chlorine and bromine, while if the other low-field band is assigned, the shifts

¹⁶ K. L. Williamson, Y.-F. Li Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, 1968, **90**, 6717; A. M. Ilrig and S. L. Smith, *ibid.*, 1970, **92**, 759.

¹⁷ R. J. Abraham, *J. Chem. Soc. (B)*, 1969, 1022.

are 4.4 and 7.3 p.p.m. The former values appear on the large size, the latter small. However, there is a coupling common to the band to highest field, assigned to F-1, and the band to lowest field, which is distinctly larger than any other coupling between bridgehead and CFX fluorines. It is therefore suggested that this involves the unique *exo*-fluorine (F-2). There remain the individual assignments of F-5 and F-6. The one chosen is based upon the assumption that for the couplings between *endo*-fluorines, $|^4J| > |^5J|$. Thus the n.m.r. parameters of Table 6 are obtained. Some

TABLE 6

N.m.r. parameters (δ in p.p.m.; J in Hz) of the tetrahalogenobicyclo[2,2,0]hexanes

X	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6		
Cl	95.1	31.3	37.6	82.9	41.9	43.0		
Br	81.3	19.6	31.7	61.4	39.1	40.0		
	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{1,5}$	$J_{1,6}$	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$
Cl	8.0	4.7	27.2	3.8	6.0	11.2	3.8	≤ 0.3
Br	12.5	4.2	23.6	1.9	3.8	22.3	5.2	≤ 0.3
	$J_{2,6}$	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	
Cl	1.2	3.0	40.8	23.0	6.1	4.9	10.2	
Br	3.8	1.8	39.5	25.0	4.1	2.0	11.9	

indirect support for the correctness of the above assignment is provided by the deceptively simple A_4X_2 nature of the spectra of the all-*exo*-isomers. This may arise when $|J_{AX} - J_{AX'}|$ is small (compare the magnitudes of $J_{4,5}$ and $J_{4,6}$ of Table 6 with $|J_{AX} + J_{AX'}|$) and J_{AA} and J_{XX} are large.

Abraham¹⁷ has considered the orientation and sign-dependence of $^4J_{F,F}$ coupling constants and argued that, within a propane-type fragment, coupling between *trans,gauche* fluorines should be small (*ca.* 0 Hz) and between eclipsed fluorines should be large (+26 Hz). The value of $J_{2,5}$ (1.2—3.8 Hz) corresponds approximately to the former, and $J_{3,5}$ (39.5—40.8 Hz) approximates to the latter. The large magnitude of $^5J_{3,6}$ (23—25 Hz) also may be indication of a through-space mechanism¹⁸ of couplings of proximate *endo*-fluorines.

The coupling between bridgehead fluorines ($J_{1,4}$) is substantial (23.6—27.2 Hz) in the bicyclohexanes, small in the bicyclohex-2-enes (0—2.5 Hz) and again appreciable (7—14.5 Hz) in the bicyclohexa-2,5-dienes.

I.r. Spectra.—Camaggi and Gozzo⁵ have noted that the CF=CF stretching frequencies in some polyfluorobicyclo[2,2,0]hexa-2,5-dienes and the derived dibromides, which occur in the range 1752—1780 cm^{-1} , are close to the values found in polyfluoronorbornenes;¹⁹ a strong :C-F stretching frequency is found in the range 1340—1370 cm^{-1} . Shown in Table 7 are C=C and :C-F stretching frequencies for a number of 2-substituted pentafluorobicyclo[2,2,0]hexa-2,5-dienes in the vapour phase.

The CF=CF stretching frequencies may be compared with those reported for polyfluoronorbornenes¹⁹ (1755—

¹⁸ For some recent examples, see K. L. Servis and K. N. Fang, *J. Amer. Chem. Soc.*, 1968, **90**, 6712; R. D. Chambers, L. H. Sutcliffe, and G. J. T. Tiddy, *Trans. Faraday Soc.*, 1970, **66**, 1025.

¹⁹ S. F. Campbell, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 1965, **21**, 2997.

1763) and perfluorocyclo-butene²⁰ (1799), -pentene²¹ (1771), and -hexene²² (1746 cm⁻¹). They are closer to

TABLE 7

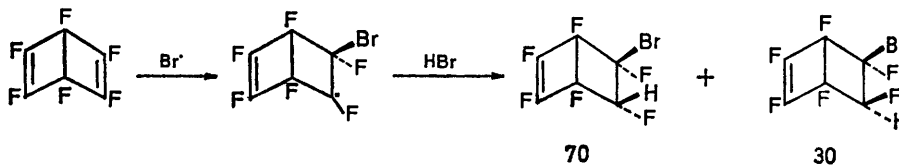
Stretching frequencies (cm⁻¹) of 2-substituted pentafluoro-bicyclo[2,2,0]hexa-2,5-dienes

2-Substituent	CF=CF	CF=CX	C-F
H	1754, 1748	1652	1348
OMe	1763	1734	1344, 1332
Me	1759	1726, 1720	1344, 1342
NMe ₂	1750, 1780	1722	1328

that of perfluorocyclohexene than to that of perfluorocyclobutene, and this is also reflected in the CF:CF stretching frequencies.²¹⁻²³ The CF=CF stretching frequencies of the polyfluorobicyclo[2,2,0]hex-2-enes (see Experimental section) occur in the range 1751–1764 cm⁻¹, similar to that for the hexadienes. It may be that this unusual range is associated with an increase in C=C-C and reduction in C=C-F bond angles compared with perfluorocyclobutene. This would lead to an increase in the contribution from C-C compression and reduction from that associated with C-F, leading to a reduction in C=C stretching frequency.²⁴ There is evidence that the 1,4-bond in hexamethylbicyclo[2,2,0]hexa-2,5-diene is unusually long,²⁵ but a preliminary electron-diffraction study²⁶ of the hexafluoro-compound has not shown this.

CONCLUSION

The present and previous studies^{1,5-7} of the reactions of hexafluorobicyclo[2,2,0]hexa-2,5-diene have revealed its chemical versatility. One or two fluorine atoms may be displaced by moderately active nucleophilic reagents, and in free-radical attack (and this may well include halogenation), attack from the *exo*-side is



apparently favoured, hydrogen bromide giving, for example, only the products of *exo*-attack by bromine atom.

In halogenations, the second molecule of halogen apparently adds exclusively *cis,exo*, and the intermediate *cis,exo*-dihalide is more reactive than the *trans*-dihalide. Catalytic hydrogenation, which may be controlled at the dihydro-stage, occurs from the *exo*-side.

This preference for *exo*-attack upon hexafluorobicyclo[2,2,0]hexa-2,5-diene is also shown in its reactions with dienes¹ and 1,3-dipoles.⁷

²⁰ G. Fuller and J. C. Tatlow, *J. Chem. Soc.*, 1961, 3198.

²¹ J. K. Brown and K. J. Morgan, *Adv. Fluorine Chem.*, 1965, 4, 270.

²² J. Burdon and D. H. Whiffen, *Spectrochim. Acta*, 1958, 12, 139.

²³ R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Org. Chem.*, 1965, 30, 3524; W. R. Cullen and P. S. Dhaliwal, *Canad. J. Chem.*, 1967, 45, 719; L. F. Thomas, unpublished work, quoted in A. B. Crayton, J. Roylance, D. R. Sayers, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 7358.

EXPERIMENTAL

Techniques similar to those used previously were employed.¹ Analytical g.l.c. was carried out with a Pye Series 104 model 24 fractometer (flame-ionization detector), and molar (%) compositions were estimated by triangulation from peak areas, supported by calibration whenever possible. Small-scale preparative g.l.c. separations were effected with either a Perkin-Elmer Fraktometer (model 451) or a Pye (model 104 or 105) instrument; and larger-scale separations were performed with a Wilkins' Aerograph Autoprep (model A700) instrument.

WARNING. The bicyclohexadiene, and probably its substituted derivatives, may explode violently, particularly around the solid-liquid phase change. It was stored at low temperatures (−78°), and handled, where possible, as the vapour at low pressures, or in solution. Heavy blast-screens were employed.

Some difficulty was experienced in obtaining consistent analytical figures for some substituted bicyclo[2,2,0]hexa-2,5-dienes, possibly owing to their thermal instability resulting in incomplete combustion. They were, however, always characterized by other physical methods.

Addition Reactions of Hexafluorobicyclo[2,2,0]hexa-2,5-diene.—(a) *With chlorine* (by R. HUBBARD). (i) 1:1 molar ratio. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.80 g, 4.3 mmol) and chlorine (0.32 g, 4.5 mmol), kept in the dark in a sealed Pyrex tube (100 ml) at room temperature for 0.5 h, gave, after fractionation, *in vacuo*, unchanged bicyclohexadiene (0.05 g, 0.3 mmol, 6% recovery), containing a trace of hexafluorobenzene, and 5,6-dichlorohexafluorobicyclo[2,2,0]hex-2-ene (1.00 g, 3.9 mmol, 90% yield) [Found: C, 27.8%; M, 257 (mass spec.). C₆Cl₂F₆ requires C, 28.0%; M, 257], ν_{\max} , 1754 cm⁻¹ (C=C str.), shown by ¹⁹F n.m.r. spectroscopy to consist of the *exo*- and *trans*-dichloroisomers in the ratio 48:52. A trace of liquid, shown by i.r. spectroscopy to be 2,3,5,6-tetrachlorohexafluorobicyclo[2,2,0]hexanes, remained in the tube.

(ii) *With an excess of chlorine.* Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.50 g, 2.7 mmol) and chlorine (0.75 g, 10.5 mmol), kept in the light at room temperature for 4 weeks, gave 2,3,5,6-tetrachlorohexafluorobicyclo[2,2,0]hexane (0.60 g, 1.8 mmol, 68% yield) (Found: C, 22.2. C₆Cl₄F₆ requires C, 21.9%), shown by ¹⁹F n.m.r. spectroscopy to consist of the *exo*-2,3,5,6/- [with ¹⁹F n.m.r. absorptions at 42.0 (CFCl) and 83.4 p.p.m., |J + J'| = 10.9 Hz] and *exo*-2,3,5/*endo*-6-tetrachloroisomers in equimolar ratio. A black involatile solid residue (0.10 g) remained.

(b) *With bromine.* (i) 1:1 molar ratio. Bromine (0.80 g, 5.0 mmol) was added dropwise to a solution of hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.95 g, 5.1 mmol), in hexafluorobenzene (20 ml), with irradiation from a 100 W tungsten filament lamp. Fractionation *in vacuo* gave

²⁴ L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, 1968, ch. 2.

²⁵ M. J. Cardillo and S. H. Bauer, *J. Amer. Chem. Soc.*, 1970, 92, 2399.

²⁶ B. Anderson, H. M. Seip, and B. Beagley, *Acta Chem. Scand.*, 1969, 23, 1837.

5,6-dibromohexafluorobicyclo[2,2,0]hex-2-ene (1.50 g, 4.4 mmol, 85% yield) [Found: C, 20.3; Br, 46.2%; *M*, 344 (mass spec.). Calc. for $C_6Br_2F_6$: C, 20.8; Br, 46.2%; *M*, 344], condensing at -23° , which was shown by g.l.c. to consist of two components in the ratio 32 : 68. A sample (0.20 g) separated by g.l.c. (8 m 20% Apiezon L on Celite at 172°) was shown by ^{19}F n.m.r. spectroscopy to consist of the *trans*-5,6-dibromo-isomer (0.04 g), ν_{\max} 1760 (C=C str.) and 1370 cm^{-1} (C-F str.), and the *exo*-5,6-dibromo-isomer (0.12 g), ν_{\max} 1760 (C=C str.) and 1370 cm^{-1} (C-F str.), in order of increasing retention time.

(ii) 1 : 2 molar ratio. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.30 g, 1.6 mmol) and bromine (0.57 g, 3.6 mmol) in trichlorofluoromethane (0.2 ml) gave (estimated by n.m.r. spectroscopy) after 1 week in the dark at room temperature, the *exo*- and *trans*-5,6-dibromohexafluorobicyclo[2,2,0]hex-2-enes (100%), in the ratio 70 : 30. The mixture was then irradiated with light from a 500 W tungsten filament lamp, and examined periodically by n.m.r. spectroscopy. After 6 h, all the *exo*- and *ca.* 80% of the *trans*-dibromide had reacted. After 48 h irradiation, the solution was shown by ^{19}F n.m.r. spectroscopy to contain a mixture of *exo*-2,3,5,6/- [with ^{19}F n.m.r. absorptions at 39.0 (CFBr) and 61.5 p.p.m., $|J + J'| = 6.9$ Hz] and *exo*-2,3,5/*endo*-6-tetra-bromohexafluorobicyclo[2,2,0]hexanes, in the ratio 70 : 30. The product from a similar reaction, after one recrystallization from aqueous ethanol, contained only the *exo*-2,3,5,6/-tetrabromide, m.p. 47.5° (lit.⁵ 47.5°).

(c) *With hydrogen*. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.50 g, 2.7 mmol) in diethyl ether (20 ml), containing 5% palladium-carbon (0.1 g), was stirred at -30° for 2 h in the presence of hydrogen (78.4 ml, 3.5 mmol) at an initial pressure of *ca.* 0.5 atmos. The volatile material was fractionated *in vacuo* to give *exo*-5*H*,6*H*-hexafluorobicyclo[2,2,0]hex-2-ene (0.04 g, 0.2 mmol, 8%) [Found: C, 38.6; H, 1.3%; *M*, 188 (mass spec.). $C_6H_2F_6$ requires C, 38.3; H, 1.1%; *M*, 188], m.p. 28° , ν_{\max} 1757 (C=C str.) and 1380 cm^{-1} (C-F str.), which condensed at -45° . The residue was extracted with chloroform (3×10 ml), the solvent was removed *in vacuo*, and the remaining solid was sublimed (45° at 0.1 mmHg) to give *exo*-2*H*,3*H*,5*H*,6*H*-hexafluorobicyclo[2,2,0]hexane (0.32 g, 1.6 mmol, 59%), m.p. $90-91^\circ$ (lit.⁵ $90-91^\circ$), spectroscopically identical to that previously reported.

A similar reaction, carried out at -50° for 8 h, gave *exo*-5*H*,6*H*-hexafluorobicyclo[2,2,0]hex-2-ene (0.30 g, 1.6 mmol, 59%) and *exo*-2*H*,3*H*,5*H*,6*H*-hexafluorobicyclo[2,2,0]hexane (0.03 g, 0.2 mmol, 6%).

(d) *With hydrogen bromide*. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (1.07 g, 5.75 mmol) and hydrogen bromide (0.466 g, 5.75 mmol), sealed in a silica tube (60 ml) and irradiated with u.v. light (Hanovia U.V.S.500 at a distance of 30 cm), gave a fraction (1.46 g) condensing at -95° *in vacuo* which was shown by g.l.c. to contain two major components and traces of hexafluorobenzene and four unidentified minor components (total < 6%). The fraction was separated by g.l.c. (4 m didecyl phthalate on Celite at 100°) to give *exo*-5*H*,*exo*-6-bromohexafluorobicyclo[2,2,0]hex-2-ene (0.97 g, 3.63 mmol, 63%) [Found: C, 27.2; H, 0.4. C_6HBrF_6 requires C, 27.0; H, 0.4%], b.p. 105.5° at 751 mmHg (Siwoloboff), ν_{\max} 1754 (C=C str.) and 1383 cm^{-1} (C-F str.), and *endo*-5*H*,*exo*-6-bromohexafluorobicyclo[2,2,0]hex-2-ene (0.41 g, 1.54 mmol, 27%) [Found: C, 27.1; H, 0.4%; *M*, 267 (mass spec.). C_6HBrF_6 requires C, 27.0; H, 0.4%; *M*, 267], b.p. 112° at 751 mmHg (Siwoloboff),

ν_{\max} 1751 (C=C str.) and 1374 cm^{-1} (C-F str.), both identified by i.r. and n.m.r. spectroscopy.

A similar reaction, carried out in the dark at 20° for 3 h, gave only unchanged reactants.

(e) *With bistrifluoromethyl nitroxide*. (i) 1 : 2 molar ratio. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.478 g, 2.57 mmol) and bistrifluoromethyl nitroxide (0.877 g, 5.22 mmol), kept in a sealed Pyrex tube (250 ml) in the dark at 20° for 18 h, gave, after fractionation *in vacuo*, perfluoro-{5,6-bis(dimethylamino-oxy)bicyclo[2,2,0]hex-2-ene} (1.07 g, 2.05 mmol, 80%) [Found: C, 22.8; N, 5.5. $C_{10}F_{18}N_2O_2$ requires C, 23.0; N, 5.4%], n_D^{24} 1.3140, b.p. 145° at 757 mmHg (Siwoloboff), ν_{\max} 1764 (C=C str.) and 1378 cm^{-1} (C-F str.), which was shown by g.l.c. (8 m Silicone oil on Celite at 50°) and ^{19}F n.m.r. spectroscopy to consist of the *exo*- and *trans*-5,6-disubstituted isomers, in the ratio 61 : 39. A trace of high-boiling liquid (0.05 g, 2%), which remained in the tube, was shown by i.r. spectroscopy to be perfluoro-{2,3,5,6-tetrakis(dimethylamino-oxy)bicyclo[2,2,0]hexane}. A similar reaction mixture in which the reactants were largely in the liquid phase (5 ml tube) exploded violently upon warming to room temperature.

(ii) 1 : 4 molar ratio. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.478 g, 2.57 mmol) and bistrifluoromethyl nitroxide (1.80 g, 10.72 mmol), kept in a sealed Pyrex tube (250 ml) in the dark at 20° for 20 days, gave, after removal of volatile material at room temperature *in vacuo*, perfluoro-{2,3,5,6-tetrakis(dimethylamino-oxy)bicyclo[2,2,0]hexane} (1.84 g, 2.14 mmol, 83%) [Found: C, 19.8; N, 6.3. $C_{14}F_{30}N_4O_4$ requires C, 19.6; N, 6.5%], b.p. 185° at 753 mmHg (Siwoloboff), n_D^{24} 1.3100, which was shown by ^{19}F n.m.r. spectroscopy to be largely the *exo*-2,3,5,6-tetra-substituted isomer (75%) [absorptions at -9.9 (CF₂), 42.4 (CFO), and 109.3 p.p.m.], and to contain, probably, two other isomers.

Nucleophilic Substitution Reactions of Hexafluorobicyclo[2,2,0]hexa-2,5-diene.—(a) *With sodium methoxide*. (i) 1 : 1 molar ratio. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (1.00 g, 5.4 mmol), shaken *in vacuo* with a suspension of sodium methoxide (0.30 g, 5.4 mmol) in diethyl ether (20 ml) at room temperature for 18 h, gave, after fractionation *in vacuo*, 2-methoxy-pentafluorobicyclo[2,2,0]hexa-2,5-diene (0.90 g, 4.6 mmol, 85%) [Found: C, 41.9; H, 2.0%; *M*, 198 (mass spec.). $C_7H_3F_5O$ requires C, 42.4; H, 1.6%; *M*, 198], b.p. 101° (isoteniscope), condensing at -45° , which was identified by i.r. and n.m.r. spectroscopy and mass spectrometry. Its vapour pressure is given by the equation $\log_{10} p$ (mm) = $6.800 - 8460/2.303RT$, whence the latent heat of vaporization is 8460 cal mol⁻¹ and Trouton's constant is 22.5 cal mol⁻¹ deg⁻¹.

(ii) 2 : 1 molar ratio. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.50 g, 2.7 mmol), was shaken *in vacuo* with a suspension of sodium methoxide (0.34 g, 6.3 mmol) in dichloromethane (20 ml) at room temperature for 60 h. The material volatile at room temperature was fractionated *in vacuo* to give 2-methoxy-pentafluorobicyclo[2,2,0]hexa-2,5-diene (0.05 g, 0.2 mmol, 9%). The residue was warmed to *ca.* 50° *in vacuo* to give a colourless liquid, which was shown by i.r. and n.m.r. spectroscopy to be a mixture of 2,5- and 2,6-dimethoxytetrafluorobicyclo[2,2,0]hexa-2,5-dienes (0.30 g, 1.4 mmol, 53%) [Found: C, 44.2; H, 3.0%; *M*, 210 (mass spec.). Calc. for $C_6H_4F_4O_2$: C, 45.7; H, 2.9%; *M*, 210]. The 2,5-dimethoxy-compound showed two bands at 58.3 (F-3, -6) and 109.5 p.p.m. (F-1, -4) in its ^{19}F n.m.r. spectrum.

(b) *With dimethylamine.* (i) 2:1 molar ratio. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.50 g, 2.7 mmol) and dimethylamine (0.24 g, 5.4 mmol) in diethyl ether (20 ml), warmed slowly from -23° to room temperature during 18 h, gave, after fractionation of the volatile material *in vacuo*, 2-(dimethylamino)pentafluorobicyclo[2,2,0]hexa-2,5-diene (0.35 g, 1.7 mmol, 62%) [Found: C, 43.3, 46.3; H, 3.1, 3.6%; M, 211 (mass spec.). $C_8H_6F_5N$ requires C, 45.5; H, 2.9%; M, 211], condensing at -45° , which was identified by i.r. and n.m.r. spectroscopy, and mass spectrometry. It darkened rapidly at room temperature to give a dark brown tar.

(ii) 4:1 molar ratio. Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.50 g, 2.7 mmol) and dimethylamine (0.48 g, 10.8 mmol) in diethyl ether (30 ml), warmed slowly from -23° to room temperature during 18 h, gave, after removal of volatile material at room temperature *in vacuo*, a dark brown residue, which was warmed *in vacuo* to give a liquid, which rapidly gave a dark intractable tar.

(c) *With methyl-lithium.* Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.50 g, 2.7 mmol) and methyl-lithium [from lithium (0.050 g, 7.1 mg atom) and iodomethane (0.50 g, 3.5 mmol) in diethyl ether (20 ml)] were warmed, with stirring, from -50° to room temperature during 12 h. The resulting solution was poured into water, the ether layer was separated, the aqueous layer was extracted with ether (3×5 ml), and the combined ethereal extracts were dried ($MgSO_4$) and fractionated *in vacuo* to give 2-methyl-pentafluorobicyclo[2,2,0]hexa-2,5-diene (0.30 g, 1.6 mmol, 61%) [Found: C, 46.0; H, 1.6%; M, 182 (mass spec.). $C_7H_3F_5$ requires C, 46.1; H, 1.65%; M, 182], condensing at -63° , which was identified by i.r. and n.m.r. spectroscopy, and mass spectrometry.

(d) *With methylmagnesium iodide.* A similar reaction in which methylmagnesium iodide, at room temperature for 18 h, instead of methyl-lithium, was used gave 2-methyl-pentafluorobicyclo[2,2,0]hexa-2,5-diene (0.03 g, 0.2 mmol, 6%).

(e) *With sodium borohydride* (with M. J. KERSHAW). Hexafluorobicyclo[2,2,0]hexa-2,5-diene (1.80 g, 13.9 mmol) was stirred with a suspension of sodium borohydride (0.24 g, 6.4 mmol) in bis-(2-methoxyethyl) ether (20 ml) at 0° for 14 h; the volatile material (1.5 g) was then shown by g.l.c. and n.m.r. spectroscopy to contain 2*H*-pentafluorobicyclo[2,2,0]hexa-2,5-diene (XIX) (80%), together with unchanged starting material and traces of penta- and hexafluorobenzene. The 2*H*-hexadiene was separated by g.l.c. (5 m Apiezon L at 48°) and identified by i.r. and n.m.r. spectroscopy.⁵

A similar reaction, in which hexafluorobicyclo[2,2,0]hexa-2,5-diene (1.00 g, 5.39 mmol) and sodium borohydride (0.127 g, 3.36 mmol) were used, gave a product (0.90 g) containing (g.l.c. and n.m.r. spectroscopy) 1,2,4,6-tetrafluorobicyclo[2,2,0]hexa-2,5-diene (XX) (80%), 1,2,3,5-tetrafluorobenzene (15%), and traces of 1*H*-pentafluorobicyclo[2,2,0]hexadiene and hexa- and penta-fluorobenzenes. The tetrafluorohexadiene (Found: C, 48.1; H, 1.6%; M, 151. $C_6H_2F_4$ requires C, 48.0; H, 1.3%; M, 150), was separated by g.l.c. and identified by i.r. and n.m.r. spectroscopy.

Reactions with a higher proportion of sodium borohydride gave product containing increasing amounts of 1,2,4-trifluorobicyclo[2,2,0]hexa-2,5-diene.⁵ For example, a reaction with 0.89 mol. equiv. of sodium borohydride gave product containing hexadiene (XX) (65%), tetrafluorobenzene (18%), and trifluorohexadiene (17%).

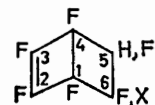
(f) *With potassium benzenethiolate.* Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.50 g, 2.7 mmol) and a suspension of potassium benzenethiolate (0.80 g, 5.4 mmol), in diethyl ether (20 ml), were shaken at room temperature for 18 h, the solvent was removed *in vacuo*, and the residue was extracted with chloroform (3×10 ml). The chloroform was removed *in vacuo* leaving 2,5-bisphenylthiotetrafluorobicyclo[2,2,0]hexa-2,5-diene (0.80 g, 2.2 mmol, 82%) [Found: C, 59.4; H, 2.8%; M, 366 (mass spec.). $C_{18}H_{10}F_4S_2$ requires C, 59.0; H, 2.7%; M, 366], m.p. $62-63^{\circ}$ (from aqueous ethanol), ν_{max} , 1743 (C=C str.) and 1370 cm^{-1} (C-F str.), which was identified by i.r. and n.m.r. spectroscopy and mass spectrometry.

A similar reaction of hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.50 g, 2.7 mmol) with potassium benzenethiolate (0.40 g, 2.7 mmol) in diethyl ether (20 ml) at -50° to -10° during 2 h, and at 0° overnight, gave unchanged bicyclohexadiene and 2,5-bisphenylthiotetrafluorobicyclo[2,2,0]hexa-2,5-diene (0.20 g, 0.6 mmol, 20%). No monophenylthio-compound was detected.

2,5-Bisphenylthiotetrafluorobicyclo[2,2,0]hexa-2,5-diene in carbon tetrachloride was completely isomerized to 1,4-bisphenylthiotetrafluorobenzene in 2 weeks at room temperature, as determined by n.m.r. spectroscopy.

(g) *With lithium halides in dimethylformamide.* Solutions of hexafluorobicyclo[2,2,0]hexadiene (0.10 g, 0.5 mmol) and lithium halide (0.5 mmol) in dimethylformamide (0.35–0.5 ml) were sealed in n.m.r. tubes at room temperature and examined periodically by ^{19}F n.m.r. spectroscopy. With lithium bromide and iodide, absorption bands due to the respective halogenopentafluorobenzenes slowly appeared (ca. 30% yield after 2 months) in addition to those of the starting material and hexafluorobenzene, which was formed in a competing isomerization. With lithium chloride, chloropentafluorobenzene (ca. 30% after 1 month) was formed, but in addition very weak bands (<5%) appeared in the regions expected for olefinic and bridgehead fluorines of a bicyclo[2,2,0]hexa-2,5-diene. However, attempts to isolate such a bicyclohexadiene from a larger scale reaction produced only chloropentafluorobenzene.

(h) *With lithium chloride in tetrahydrofuran.* Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.50 g, 2.7 mmol) and lithium chloride (0.10 g, 2.7 mmol) in tetrahydrofuran (20 ml), kept *in vacuo* at room temperature for 2 months, gave, after fractionation *in vacuo*, a colourless liquid fraction, condensing at -23° , which was tentatively identified on the basis of i.r. and n.m.r. spectroscopy, and mass spectrometry, as 5*H*-6-(tetrahydrofuran-2-yl)hexafluorobicyclo[2,2,0]hex-2-ene (0.25 g, 1.0 mmol, 36%), as a mixture of two isomers in the ratio 1:1.8, ν_{max} , 2956, 2874 (C-H str.), 1773 (FC=CF str.), and 1746 cm^{-1} (FC=C str.). Its 1H n.m.r. spectrum showed bands at τ 4.6 (CHF; a



X=tetrahydrofuran-2-yl

geminal H,F coupling of ca. 50 Hz was apparent), 5.8 (CH-O), 6.2 (CH₂-O), and 8.0 (C-CH₂-CH₂-C) of appropriate intensities. In the ^{19}F n.m.r. spectrum (at 94.08 MHz), bands assigned to the major isomer appeared at 42.5

(intensity 2, F-2 and F-3), 101.5, 102.8 (F-1 and F-4), 112.0 (F-6), and 123.2 p.p.m. (F-5, d, $J_{\text{H,F-gem}}$ ca. 50 Hz), and to the minor isomer at 41.6, 43.1 (F-2 and F-3), 103.6, 106.6 (F-1 and F-4), 112.4 (F-6), and 121.3 p.p.m. (F-5). The mass spectrum showed m/e 258 (M^+ , 0.2%), and a base peak corresponding to $\text{C}_4\text{H}_7\text{O}^+$.

Reaction of Hexafluorobicyclo[2,2,0]hexa-2,5-diene with Caesium Fluoride in Formamide.—Hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.506 g, 2.72 mmol), caesium fluoride (1.10 g, 8.26 mmol), and formamide (2 ml) were sealed in a Pyrex tube (10 ml) and shaken at 50° for 9 h. The product (0.26 g) volatile at room temperature was separated by g.l.c. (dinonyl phthalate, 4 m, at 60°) to give unchanged hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.096 g, 0.52 mmol, 19% recovery), hexafluorobenzene (0.031 g, 0.17 mmol), *exo*-5H-heptafluorobicyclo[2,2,0]hex-2-ene (0.122 g, 0.59 mmol, 27% yield based on hexadiene consumed) [Found: C, 34.8; H, 0.6%; M , 206 (mass spec.). C_6HF_7 , requires C, 35.0; H, 0.5%; M , 206], which was identified by i.r. and n.m.r. spectroscopy, and possibly *endo*-5H-heptafluorobicyclo[2,2,0]hex-2-ene (0.010 g, 0.05 mmol, 2%), identified by n.m.r. spectroscopy.

*Dehydrobromination of *exo*-5H,*exo*-6-Bromohexafluorobicyclo[2,2,0]hex-2-ene.*—*exo*-5H,*exo*-6-Bromohexafluorobicyclo[2,2,0]hex-2-ene (0.077 g, 0.288 mmol) and potassium hydroxide pellets (5 g), kept in a sealed Pyrex tube (10 ml) at 20° for 20 h, gave hexafluorobicyclo[2,2,0]hexa-2,5-diene (0.036 g, 0.194 mmol, 67%), which was identified by i.r. spectroscopy.

*Attempted Dehydrofluorination of *exo*-5H,6H/-Hexafluoro-*

bicyclo[2,2,0]hex-2-ene.—*exo*-5H,6H/-Hexafluorobicyclo[2,2,0]hex-2-ene (0.14 g, 0.7 mmol) was shaken *in vacuo* with a solution of potassium hydroxide (0.3 g) in water (0.5 ml) at room temperature for 24 h. Hexene (0.10 g, 0.5 mmol, 73%) was recovered from the dark brown aqueous solution, and no water-insoluble products were observed.

The hexene was unaffected (100% recovery) by powdered potassium hydroxide during 20 h at 30°.

Bromination of 2-Methoxypentafluoro[2,2,0]hexa-2,5-diene.—Bromine (0.40 g, 2.5 mmol) was added to a solution of 2-methoxypentafluorobicyclo[2,2,0]hexa-2,5-diene (0.60 g, 3.0 mmol) in dichloromethane (10 ml), and the solution was kept at room temperature for 8 h in daylight. Fractionation, *in vacuo*, of the material volatile at room temperature gave unchanged hexadiene (0.1 g, 0.5 mmol, 17%). The residue was distilled *in vacuo* (ca. 70° bath temp.) to give a mixture of isomeric 5,6-dibromo-5-methoxypentafluorobicyclo[2,2,0]hex-2-enes (0.8 g, 2.2 mmol, 74%) [Found: C, 24.0; H, 1.0%; M , 356 (mass spec.). Calc. for $\text{C}_7\text{H}_3\text{Br}_2\text{F}_5\text{O}$: C, 23.5; H, 0.9%; M , 356], b.p. 172° at 760 mmHg (Siwoloboff), ν_{max} 1758 cm^{-1} (CF·CF str.). The ^{19}F n.m.r. spectrum (in CCl_4) indicated that it was largely the *exo*-5,6-dibromo-isomer, showing five absorption bands of equal intensity at 35.6 (CFBr), 41.5, 42.8 (CF·CF), 93.8 [CF·CBr(OMe)], and 99.3 p.p.m. (CF·CFBr), since the chemical shifts of the olefinic and bridgehead fluorines were similar to those of the corresponding fluorine nuclei in *exo*-5,6-dibromohexafluorobicyclo[2,2,0]hex-2-ene (II; X = Br).

[1/1473 Received, 16th August, 1971]