Valence-bond Isomer Chemistry. Part VII.[1] Photochemical Interconversion of the Perfluoroxylenes

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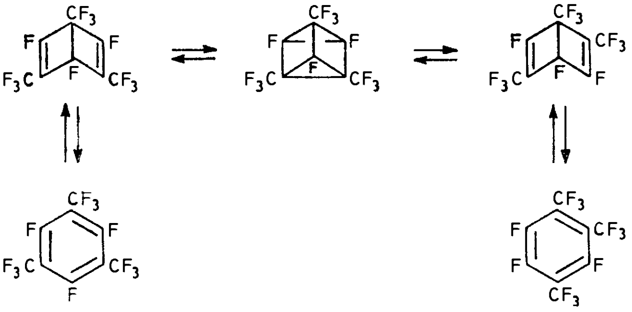
U.v. irradiation in the vapour phase interconverts the perfluoroxylenes, with perfluoro-*o*-xylene the most photochemically reactive, and perfluoro-*p*-xylene the least. The process probably occurs *via para*-bonded and prismane valence-bond isomers, and of the possible six isomers of the former type, perfluoro-1,2-, 1,3-, and -2,5-dimethylbicyclo[2.2.0]hexa-2,5-diene have been characterised, and the 2,3- and 2,6-isomers tentatively identified.

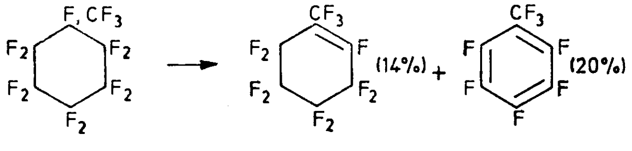
Perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene undergoes the expected addition of bromine to the CF:CF bond, and substitution by sodium methoxide of the fluorine atom of the CF:C·CF$_3$ double bond.

PERFLUORO-1,3,5- AND -1,2,4-TRIMETHYLBENZENES are interconvertible, by u.v. irradiation, *via para*-bonded and unstable prismane isomers[1] (Scheme 1). This process, formally involving a shift of alkyl groups, has been often observed, but the intermediates have largely proved elusive. We now report a comparable study of the perfluoroxylenes.



SCHEME 1

The perfluoroxylenes were prepared (*ca.* 40%) by the reductive defluorination of perfluorodimethylcyclohexanes over tri-iron tetraoxide. This was complicated by two factors, in that some partial defluorination occurred—indeed in a comparable defluorination of perfluoromethylcyclohexane (Scheme 2) perfluoro-1-methylcyclohexene was isolated—and the product was not isomerically pure. The lack of purity was due in part to isomeric contaminants in the starting cyclohexane. For example, a sample of perfluoro-1,3-dimethylcyclohexane, containing 1,2- (8%) and 1,4-isomers (7%), gave perfluoroxylenes (44%) containing *ortho*-, *meta*-, and *para*-isomers in the ratio 2 : 91 : 7, but the proportions of isomeric product formed indicated that either selective destruction of a particular cyclohexane was taking place during defluorination, or, less likely, isomerisation was occurring. Although isomerisation during defluorination over metal surfaces has been reported,[2] the isomeric purity of the starting cyclohexanes was not stated, and clear proof of isomerisation is not yet available.



SCHEME 2

Vapour-phase u.v. irradiation of perfluoro-*m*-xylene (I), led to perfluoro-*o*- (IX) and *p*-xylenes (V), the *para*-bonded benzenes perfluoro-1,2- (X) and -1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (II), and, tentatively identified, in trace amounts, perfluoro-2,6-dimethylbicyclo-[2.2.0]hexa-2,5-diene (XII). Perfluoro-*o*-xylene, which was the most readily isomerised, gave substantial amounts of *m*- and *p*-xylenes, the 1,2- and 1,3-hexadienes (X) and (II), and small amounts of a component tentatively identified as perfluoro-2,3-dimethylbicyclo[2.2.0]-hexa-2,5-diene (VIII). Perfluoro-*p*-xylene was much more photochemically stable than its isomers, produced little or no isomeric xylenes, but gave five more volatile components which, in order of increasing g.l.c. retention times, were obtained in the ratio 35 : 33 : 2 : 45 : 4. The three major components, in order of increasing retention time, were perfluoro-2,5- (IV), -1,3- (II), and -1,2-dimethylbicyclo[2.2.0]hexa-2,5-diene (X). The two minor components were not identified, but the last component had a retention time the same as that of the tentatively identified 2,6-dimethylhexadiene (XII). These observations are uniquely accommodated by Scheme 3, where interconversion of the xylenes involves six *para*-bonded benzenes and three prismanes.

The effect of wavelength of irradiation and the nature and pressure of diluent gas upon the isomerisation of perfluoro-*m*-xylene were investigated. In the presence of nitrogen (*ca.* 1 atm), decreasing wavelength resulted in increasing conversion of *m*-xylene into its isomers, and at shorter wavelengths the distribution of isomers was more widespread, probably as a result of increasing absorption by the hexadienes [the 1,2-dimethylhexadiene (X) has $\lambda_{max.}$ (vapour) 199 nm (ε 2 300) and the 1,3-dimethylhexadiene $\lambda_{max.}$ 198 nm (1 600), both with substantial tails to *ca.* 250 nm]. Isomers leading to *p*-xylene (path *a*) predominated over those leading to *o*-xylene (path *b*), but this predominance was less marked at the shortest wavelength. In comparison with argon, an inefficient acceptor of vibrational excitation,[3] nitrogen depressed the conversion and also the formation of *o*-xylene; oxygen caused increased breakdown but had

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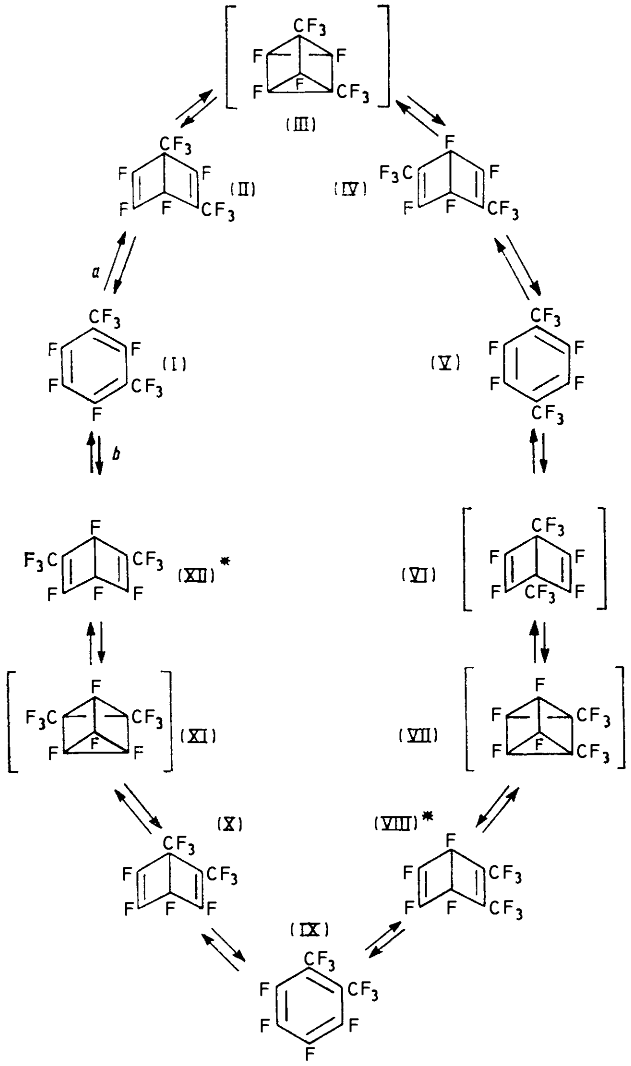
[1] Part VI, M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, *J.C.S. Perkin I*, 1974, 1736.

[2] C. R. Patrick, A. E. Pedler, A. Seabra, R. Stephens, and J. C. Tatlow, *Chem. and Ind.*, 1963, 1557.

[3] T. L. Cottrell and J. C. McCoubrey, 'Molecular Energy Transfer in Gases,' Butterworths, London, 1961.

little other effect, which argues against the involvement of triplet species. Increased pressures of argon ($\lambda > 230$ nm) resulted in an increase in isomerisation, a reduction in by-product formation, and a reduction in selectivity of isomerisation pathways, implying that vibrational deactivation, while always important, suppresses more readily the path (*a*) to *p*-xylene.



SCHEME 3
* Tentatively identified.

Nowhere was evidence found for the involvement of benzvalene isomers, and none of the three possible prismanes [(III), (VII), and (XI)] was detected. The intermediacy of prismanes is suggested by analogy with perfluoro-1,3,5- and-1,2,4-trimethylbenzenes;[1] it may be they are not true intermediates on the paths connecting pairs of bicyclohexadienes.

The perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (II) undergoes the expected reactions:[4,5] substitution at the $CF{:}C{\cdot}CF_3$ double bond by methoxide ion, and addition of bromine to the $CF{:}CF$ bond (Scheme 4). Both dibromides show a low-field shift of bridgehead fluorines in their ^{19}F n.m.r. spectra, indicating an adjacent *exo*-bromine,[5] and, on the basis of previous assignments of 5,6-dibromohexafluorobicyclo[2.2.0]hex-2-enes, the most prevalent is the *trans*-isomer, which shows substantial coupling (*J* 12.2 Hz) of bridgehead CF_3 to CFBr.

Previously it has been reported that perfluoro-*o*-xylene is isomerised by u.v. and γ-ray irradiation to perfluoro-1,2-dimethylbicyclo[2.2.0]hexa-2,5-diene (X),[6] and that u.v. irradiation of perfluoro-*p*-xylene produces, in low conversion, a complex mixture, containing six components (g.l.c.), from which it was claimed that perfluoro-1,4- (VI) and -2,5-dimethylbicyclo[2.2.0]hexa-2,5-diene (IV) were isolated.[4] However, this work is of uncertain status since the identity of the isomer (IV) was based only on mass spectrometric and i.r. data, and the ^{19}F n.m.r. chemical shifts quoted for isomer (VI) [ϕ^* 57.6 and 139.0 (ref. 7)] correspond closely to those of perfluoro-*p*-xylene itself.

The photochemical interconversions of the perfluoroxylenes resemble those of their hydrocarbon counterparts; in the latter cases however, 1,2-methyl shifts are prevalent, and benzvalene isomers,[8] as opposed to *para*-bonded isomers,[9] have been favoured as intermediates. Introduction of fluorine leads to substantial stabilisation of strained intermediates. Photoisomerisation to bicyclo[2.2.0]hexa-2,5-dienes occurs for perfluoro-benzene,[4] -toluene,[4] -xylenes, and -trimethylbenzenes,[1] whereas benzene itself isomerises to benzvalene,[10] except at short wavelengths,[11] as does hexakis(trifluoromethyl)benzene.[12] At this time, there appears no obvious explanation for this distinction.

EXPERIMENTAL

Experimental techniques were similar to those described previously.[1] ^{19}F Chemical shifts are quoted in p.p.m. to high field of external $CF_3{\cdot}CO_2H$. U.v. irradiations were carried out, for the most part, in the vapour phase in a 10 l photochemical reactor.

Preparation of Perfluoroxylenes.—The perfluoroxylenes were prepared by defluorination of perfluorodimethylcyclohexanes,* by a method similar to that described for perfluoro-1,3,5-trimethylbenzene.[1]

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* The composition of dimethylcyclohexane samples, which were not isomerically pure, was determined by a combination of ^{19}F n.m.r. spectroscopy and g.l.c. (1 m TXP + 10 m SE30 columns at 20 °C).

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

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[7] L. Cavalli, *J. Chem. Soc.* (*B*), 1970, 1616.

[8] K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1964, **86**, 2307; R. B. Cundall and A. J. R. Voss, *Chem. Comm.*, 1968, 903; 1969, 116; D. Anderson, *J. Phys. Chem.*, 1970, **74**, 1687; W. A. Noyes and D. A. Harter, *ibid.*, 1971, **75**, 2741.

[9] H. R. Ward, *J. Amer. Chem. Soc.*, 1967, **89**, 2367.

[10] K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Amer. Chem. Soc.*, 1967, **89**, 1031; K. E. Wilzbach and L. Kaplan, *ibid.*, 1968, **90**, 3291.

[11] H. R. Ward and J. S. Wishnok, *J. Amer. Chem. Soc.*, 1968, **90**, 5353.

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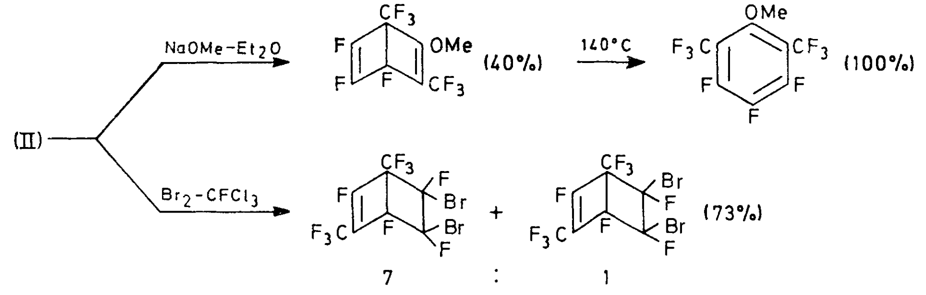
(a) *Perfluoro*-m- *and* o-*xylenes.* A mixture of perfluoro-1,3- (33.5 g, 83.7 mmol), perfluoro-1,2- (3.2 g, 8.0 mmol), and perfluoro-1,4-dimethylcyclohexane (2.8 g, 7.0 mmol) was defluorinated to give a mixture, shown by g.l.c. (10 m APL at 110 °C) and ^{19}F n.m.r. spectroscopy to comprise unchanged cyclohexanes (11.6 g, 46.5 mmol, 47%) containing partially defluorinated material, perfluoro-*m*-xylene (5.9 g, 20.6 mmol, 40% yield based on cyclohexane converted), perfluoro-*p*-xylene (0.46 g, 1.6 mmol, 3%), and perfluoro-*o*-xylene (0.13 g, 0.5 mmol, 1%).

The product of several such defluorinations was distilled (Nester–Faust 36 in spinning band) and the aromatic fraction, b.p. 125—127 °C, was separated by g.l.c. (10 m APL at 110 °C) to give a mixture of perfluoro-*m*- and *p*-xylenes in the ratio 13 : 1, and perfluoro-*o*-xylene (Found: C, 33.6; F, 66.4%; *M*, 286. Calc. for C_8F_{10}: C, 33.6; F, 66.4%; *M*, 286), b.p. 127—128 °C (lit.,[13] 128 °C).



SCHEME 4

Perfluoro-*m*- and *p*-xylenes were found not to be separable readily by g.l.c. but since the *p*-compound was much less easily photoisomerised than the *m*-compound its presence (4—6%) in the *m*-compound used for the bulk of this work provided little complication. A pure sample of the *m*-xylene was obtained by the quantitative thermal isomerisation of perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (see below) at 150 °C for 4 days (Found: C, 33.8; F, 66.2%; *M*, 286); b.p. 122—123 °C at 755 mmHg (Siwoloboff) (lit.,[14] 122—123 °C), and a pure sample of perfluoro-*p*-xylene by the reaction of sulphur tetrafluoride with tetrafluoroterephthalic acid[4] (Found: C, 33.4; F, 66.2%; *M*, 286); b.p. 121—122 °C (lit.,[13] 122 °C).

(b) *Perfluoro*-p-*xylene.* Perfluoro-1,4- (265.0 g, 663 mmol) and perfluoro-1,3-dimethylcyclohexane (14.2 g, 35 mmol) were defluorinated to give a mixture of unchanged cyclohexanes (164.8 g, 412 mmol, 59% recovery), containing some partially defluorinated material, perfluoro-*p*-xylene (28.2 g, 99 mmol, 35%), perfluoro-*m*-xylene (3.9 g, 14 mmol, 5%), and perfluoro-*o*-xylene (0.4 g, 1 mmol, 0.5%).

(c) *Perfluoro*-o-*xylene.* Perfluoro-1,2- (10.29 g, 24.7 mmol) and perfluoro-1,3-dimethylcyclohexane (2.25 g, 5.6 mmol) were defluorinated to give unchanged cyclohexanes (2.26 g, 5.7 mmol, 18% recovery), partially defluorinated material (*ca.* 2.1 g, 5 mmol, 24%), perfluoro-*m*-xylene (0.88 g, 3.1 mmol, 12%), and perfluoro-*o*-xylene (1.52 g, 5.3 mmol, 21%).

The perfluoroxylenes absorbed as follows in the u.v.: (i) *o*-xylene, $\lambda_{\text{max.}}$ (EtOH) 272 (ε 1 920), $\lambda_{\text{min.}}$ 239 (140); (ii) *m*-xylene, $\lambda_{\text{max.}}$ (C_6H_{14}) 205 (5 300) and 267 (1 330), $\lambda_{\text{min.}}$ 230 (<30); (iii) *p*-xylene, $\lambda_{\text{max.}}$ (C_6H_{14}) 209 (6 320) and 287 (3 230), $\lambda_{\text{min.}}$ 231 nm (<30).

Defluorination of Perfluoromethylcyclohexane.—Perfluoromethylcyclohexane (12.4 g, 35.4 mmol) was defluorinated to give a mixture, shown by ^{19}F n.m.r. spectroscopy and g.l.c. (10 m SE30 at 25 °C) to comprise perfluoromethylcyclohexane (3.9 g, 11.0 mmol, 31% recovery), perfluoro-1-methylcyclohexene (1.6 g, 5.0 mmol, 21%), and perfluorotoluene (1.7 g, 7.0 mmol, 29%).

A similar reaction, carried out immediately without regeneration of the tri-iron tetraoxide gave unchanged cyclohexane (39%), perfluoro-1-methylcyclohexene (27%), and perfluorotoluene (25%).

The combined products were distilled (Nester–Faust 18 in spinning band) and the more volatile fraction, b.p. 70—80 °C, was separated by g.l.c. (10 m SE30 at 20 °C) to give perfluoromethylcyclohexane and perfluoro-1-methylcyclohexene, b.p. 75—76 °C at 757 mmHg (Siwoloboff) (lit.,[15] 75 °C), identified by i.r.[16] and ^{19}F n.m.r. spectroscopy [−20.0 (CF_3), 33.1 (6-F_2), 34.7 (⁚CF), 44.0 (3-F_2), and 58.2 p.p.m. (4- and 5-F_2)].

The Perfluorodimethylbenzene Valence-bond Isomer System.—(a) *Vapour phase u.v. irradiation of a mixture of perfluoro*-m- *and* p-*xylenes.* Argon (757 mmHg), perfluoro-*m*-xylene (1.076 g, 3.76 mmol), and perfluoro-*p*-xylene (0.057 g, 0.20 mmol), contained in the photochemical reactor, were irradiated (λ > 230 nm) for 46 h. The volatile products were removed and shown by ^{19}F n.m.r. spectroscopy and g.l.c. (10 m SE30 at 30 °C for 25 min, then programmed to 110 °C at 48 °C min^{-1}) to contain perfluoro-*m*-xylene (0.403 g, 1.41 mmol, 37% recovery), perfluoro-*p*-xylene (0.066 g, 0.23 mmol, an increase corresponding to 1.3% of the *m*-xylene converted), perfluoro-*o*-xylene (0.021 g, 0.07 mmol, 3% yield based on *m*-xylene converted), perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (0.461 g, 1.61 mmol, 69% yield), perfluoro-1,2-dimethylbicyclo[2.2.0]hexa-2,5-diene (0.071 g, 0.26 mmol, 10%), and traces (<0.5%) of a component tentatively identified as perfluoro-2,6-dimethylbicyclo[2.2.0]hexa-2,5-diene (see below).

The products of several such irradiations were separated by fractional condensation *in vacuo*. The less volatile fraction was separated by g.l.c. into a mixture of perfluoro-*m*- and *p*-xylenes in the ratio 7 : 1, and perfluoro-*o*-xylene. The more volatile fraction was separated by g.l.c. (10 m SE30 at 30 °C) to yield, in order of increasing retention time, *perfluoro*-1,3-*dimethylbicyclo*[2.2.0]*hexa*-2,5-*diene* (II) (Found: C, 33.8; F, 66.0%; *M*, 286. C_8F_{10} requires C, 33.6; F, 66.4%; *M*, 286), $\nu_{\text{max.}}$ 1 777s, sh, 1 773s (CF=CF

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str.), 1 739s, sh, and 1 732s cm^{-1} (CF=C·CF$_3$ str.), $\lambda_{max.}$ (vapour) 198 nm (ε 1 600), as a liquid, b.p. 67.5 °C (isoteniscope), perfluoro-1,2-dimethylbicyclo[2.2.0]hexa-2,5-diene (X) (Found: C, 34.0; F, 66.1%; *M*, 286), $\nu_{max.}$ 1 777m, sh, 1 772m (CF=CF str.), 1 738m, sh, and 1 730s cm^{-1} (CF=C·CF$_3$ str.), $\lambda_{max.}$ 199 nm (ε 2 300), and a small amount (*ca.* 0.004 g isolated) of an impure sample of a component tentatively identified as perfluoro-2,6-dimethylbicyclo-[2.2.0]hexa-2,5-diene (XII), $\nu_{max.}$ 1 727 cm^{-1} (CF=C·CF$_3$ str.). The last component had a g.l.c. retention time similar to but distinct from those of its isomeric bicyclohexadienes, and its accumulated ^{19}F n.m.r. spectrum showed bands at −13.0 (:C·CF$_3$) and +4.8 p.p.m. (C*F*:C·CF$_3$) (the region above 100 p.p.m. was not examined). During the spectral accumulation, bands due to perfluoro-*m*-xylene appeared, and these were enhanced when the sample was heated to 35 °C for 40 h, with a corresponding reduction of bands ascribed to the hexadiene (XII).

Many similar irradiations were carried out with variations in the wavelength of light used, and in the nature and pressure of diluent gas; the results of some of these are summarised in the Table. In all cases, the *m*-xylene was contaminated with 4—6% of the rather photochemically inert perfluoro-*p*-xylene. Additional perfluoro-*p*-xylene was detected in reactions 3 and 4, and formed in substantial amounts (*ca.* 10%) in reactions 5 and 7—9.

Vapour-phase photochemical isomerisations of perfluoro-*m*-xylene

				Perfluoro-*m*-xylene [a]			Product (%) [b]		
Reaction	Wavelength (nm)	Time (h)	Diluent gas (mmHg)	Taken (g, mmol)	Recovered (g, mmol)	Conversion [g (%)]	1,3-Me$_2$-hexadiene (II)	1,2-Me$_2$-hexadiene (X)	*o*-Xylene (IX)
1	>230	45.0	Ar (50)	0.96, 3.37	0.45, 1.56	0.51 (54)	75	5	1
2	>230	45.0		1.20, 4.21	0.69, 2.42	0.51 (43)	67	3	
3	>230	45.5	Ar (757)	1.08, 3.76	0.40, 1.41	0.68 (63)	69	10	3
4	>230	69.0	N$_2$ (755)	1.31, 4.58	0.46, 1.62	0.85 (65)	68	14	2
5	>255	66.8	Ar (50)	0.93, 3.26	0.54, 1.90	0.39 (42)	81	3	<0.2
6	>255	45.0	N$_2$ (750)	0.62, 2.15	0.49, 1.71	0.13 (21)	50	7	
7	>200	45.0	N$_2$ (755)	0.69, 2.40	0.41, 1.43	0.28 (40)	43	14	10
8	>230	45.5	N$_2$ (755)	0.50, 1.76	0.28, 0.99	0.22 (44)	67	9	<0.2
9	>230	45.5	O$_2$ (755)	0.47, 1.66	0.27, 0.93	0.20 (44)	40	9	

[a] Plus 4—6% perfluoro-*p*-xylene. [b] Where 1,3-Me$_2$-hexadiene is perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene, 1,2-Me$_2$-hexadiene is perfluoro-1,2-dimethylbicyclo[2.2.0]hexa-2,5-diene, and *o*-xylene is perfluoro-*o*-xylene; product composition was determined by g.l.c. and ^{19}F n.m.r. spectroscopy, and formation of additional perfluoro-*p*-xylene was detected in certain cases.

(b) *Irradiation of pure perfluoro*-m-*xylene*. Argon (755 mmHg) and perfluoro-*m*-xylene (0.485 g, 1.70 mmol), irradiated (λ > 200 nm) for 48 h, gave perfluoro-*m*-xylene (0.203 g, 0.71 mmol, 42% recovery), perfluoro-*o*-xylene (0.015 g, 0.05 mmol, 5% yield based upon *m*-xylene converted), perfluoro-*p*-xylene (0.063 g, 0.22 mmol, 22%), the hexadiene (II) (0.108 g, 0.38 mmol, 38%), the hexadiene (X) (0.028 g, 0.10 mmol, 10%), and, tentatively identified, the hexadiene (XII) (0.004 g, 0.01 mmol, 1%).

Perfluoro-*m*-xylene, when irradiated as the liquid, or in solution in perfluoro-n-pentane or perfluorodiethyl ether, showed only low conversion (<3%) into perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene. When passed through a packed silica tube at 500 °C it was unchanged (93% recovery).

(c) *Irradiation of perfluoro*-o-*xylene*. Argon (750 mmHg) and perfluoro-*o*-xylene (0.597 g, 2.09 mmol), irradiated (λ > 200 nm) for 45 h, gave perfluoro-*o*-xylene (0.116 g, 0.41 mmol, 19% recovery), perfluoro-*m*-xylene (0.062 g, 0.22 mmol, 13% yield based upon *o*-xylene converted), perfluoro-*p*-xylene (0.071 g, 0.25 mmol, 15%), perfluoro-1,2-dimethylbicyclo[2.2.0]hexa-2,5-diene (0.240 g, 0.84 mmol, 50% yield), perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (0.020 g, 0.07 mmol, 4%), and a component (0.005 g, 0.002 mmol, 1%) which showed ^{19}F n.m.r. bands at −10.7 (:C·CF$_3$) and +46.0 p.p.m. (CF:CF), tentatively identified as perfluoro-2,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (VIII). The two major hexadienes were separated by g.l.c.

(d) *Irradiation of perfluoro*-p-*xylene*. Argon (758 mmHg) and perfluoro-*p*-xylene (0.457 g, 1.60 mmol), irradiated (λ > 200 nm) for 42 h, gave perfluoro-*p*-xylene (0.387 g, 1.35 mmol, 85% recovery), perfluoro-1,2-dimethylbicyclo-[2.2.0]hexa-2,5-diene (0.008 g, 0.03 mmol, 12% yield based upon *p*-xylene converted), perfluoro-2,5-dimethylbicyclo-[2.2.0]hexa-2,5-diene (0.006 g, 0.02 mmol, 9%), perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (0.006 g, 0.02 mmol, 8%), perfluoro-2,6-dimethylbicyclo[2.2.0]hexa-2,5-diene (0.0007 g, 0.002 mmol, 1%), and an unidentified component (*ca.* 0.0002 g) of similar volatility to the other bicyclohexadienes.

The product of several such irradiations was separated by fractional condensation *in vacuo*, and the more volatile fraction was separated by g.l.c. (10 m SE30 at 30 °C) to give, in order of increasing retention time, *perfluoro*-2,5-*dimethylbicyclo*[2.2.0]*hexa*-2,5-*diene* (IV) (Found: C, 33.9%; *M*, 286. C_8F_{10} requires C, 33.6%; *M*, 286), $\nu_{max.}$ 1 736w, sh, 1 720vs, sh, and 1 714vs cm^{-1} (CF=C·CF$_3$ str.), as a liquid, and perfluoro-1,3- and -1,2-dimethylbicyclo[2.2.0]-hexa-2,5-dienes.

The ^{19}F n.m.r. spectrum of perfluoro-2,5-dimethylbicyclo-[2.2.0]hexa-2,5-diene showed only 3 types of fluorine with bands at −14.0 (F-2 and -5), +5.2 (F-3 and -6), and 113.6 p.p.m. (F-1 and -4) and appropriate chemical shifts. In the vapour phase it is quantitatively isomerised to perfluoro-*p*-xylene in 2 h at 100 °C; this and the n.m.r. and i.r. data are all consistent with the structure proposed.

Perfluoro-*p*-xylene showed no detectable isomerisation when passed through a packed silica tube at 500 °C and 0.01 mmHg.

Properties of the Perfluorodimethylbicyclo[2.2.0]*hexa*-2,5-*dienes*.—Mass spectral data for the three xylenes and the perfluoro-1,2-, -1,3-, and -2,5-dimethylbicyclo[2.2.0]hexa-2,5-dienes have been deposited as Supplementary Publication No. SUP 21418 (3 pp.) *. In all cases, the parent ion is prominent, least so for the *o*-xylene, and the base peak for the *p*-xylene and 2,5-dimethylhexadiene. Loss of F provides the base peak for the *o*- and *m*-xylenes, and for the 1,3-dimethylhexadiene, and is very prominent for the remainder.

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* For details of Supplementary Publications, see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

Loss of CF_3 is very prominent for the *o*-xylene and the 1,2-dimethylhexadiene (base peak) with adjacent CF_3 groups, and the CF_3^+ ion is most prominent for these two compounds. Other prominent ions include $C_7F_8^+$, $C_7F_6^+$, $C_6F_6^+$, $C_7F_5^+$, $C_6F_5^+$, $C_6F_4^+$, $C_5F_3^+$, and $C_3F_3^+$, and, in general, the lighter fragment ions are more prominent for the hexadienes than for the xylenes.

The spectroscopic data for these *para*-bonded derivatives contained no surprising results or difficulties; related data have been discussed in earlier parts of this series, particularly ref. 5.

(a) *Perfluoro*-1,2-*dimethylbicyclo*[2.2.0]*hexa*-2,5-*diene*. The vapour pressure of the hexadiene (X), measured over the range 20—60 °C is given by the equation $\log_{10}(p/\mathrm{mmHg}) = 8.40 - 1\,640/(T/\mathrm{K})$ whence the calculated b.p. is 60.5 °C, the latent heat of vaporisation is 7 840 cal mol^{-1}, and Trouton's constant is 22.4 cal K^{-1} mol^{-1}. It shows ^{19}F n.m.r. absorption at −11.8 (F-2,* $J_{2,3}$ 9.3 Hz), −8.4 (F-1, $J_{1,4}$ 6.6 Hz), +9.8 (F-3), 44.1 (F-6, $J_{3,6}$ 13.1, $J_{4,6}$ 7.3, $J_{5,6}$ 4.5 Hz), 49.2 ($J_{4,5}$ 7.9, $J_{1,5}$ 2.8 Hz), and 119.8 p.p.m. (F-4) consistent with the structure proposed, as are its i.r. spectrum and isomerisation to the *o*-xylene.

Its half-life, in hexafluorobenzene solution, towards aromatisation to perfluoro-*o*-xylene, is 1.75 ± 0.2 h at 90 °C.

U.v. irradiation. The hexadiene (X) (0.116 g, 0.41 mmol) and perfluoro-n-pentane, sealed in a silica n.m.r. tube, were irradiated (>200 nm) at 20 cm from the lamp, and periodically examined by ^{19}F n.m.r. spectroscopy, which indicated initial formation of perfluoro-*o*-xylene, with some formation of *m*- and *p*-xylenes upon long-term irradiation.

(b) *Perfluoro*-1,3-*dimethylbicyclo*[2.2.0]*hexa*-2,5-*diene*. The vapour pressure of the hexadiene (II), measured over the range 20—60 °C, is given by the equation: $\log_{10}(p/\mathrm{mmHg}) = 7.48 - 1\,570/(T/\mathrm{K})$, whence the calculated b.p. is 67.5 °C, the latent heat of vaporisation is 7 180 cal mol^{-1}, and Trouton's constant is 23.2 cal K^{-1} mol^{-1}. It shows ^{19}F n.m.r. absorption at −11.3 (F-3, $J_{2,3}$ 9.6), −8.9 (F-1, $J_{1,4}$ 7.6, $J_{1,5}$ 2.7, $J_{1,6}$ 1.1, $J_{1,2}$ 0.7 Hz), +7.1 (F-2, $J_{2,5}$ 12.7, $J_{2,4}$ 5.6, $J_{2,6}$ 1.8 Hz), 45.7 (F-5, $J_{4,5}$ 7.4, $J_{5,6}$ 4.2, $J_{3,5}$ *ca.* 0.4 Hz), 47.6 (F-6), and 120.1 p.p.m. (F-4, $J_{4,6}$ 6.7, $J_{3,4}$ *ca.* 0.4 Hz) consistent with the structure proposed, as are its i.r. spectrum, thermal isomerisation to the *m*-xylene, and reaction with MeO^-.

Its half-life, in hexafluorobenzene solution, towards aromatisation to perfluoro-*m*-xylene, is 13.6 ± 0.3 h at 90 °C.

(i) *U.v. irradiation*. Nitrogen (750 mmHg) and perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (0.420 g, 1.47 mmol) were irradiated (>200 nm) for 45.5 h to give perfluoro-1,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (0.250 g, 0.87 mmol, 60% recovery), perfluoro-1,2-dimethylbicyclo-[2.2.0]hexa-2,5-diene (0.020 g, 0.07 mmol, 12% yield based upon hexadiene converted), perfluoro-*m*-xylene (0.098 g, 0.34 mmol, 58%), perfluoro-*p*-xylene (*ca.* 0.002 g, 0.007 mmol, 1%), and perfluoro-*o*-xylene (*ca.* 0.004 g, 0.014 mmol, 2%).

The hexadiene, when irradiated in perfluoro-n-pentane solution, was slowly converted into perfluoro-*m*-xylene.

(ii) *Bromination*. The hexadiene (0.795 g, 2.78 mmol), bromine (0.439 g, 2.78 mmol), and trichlorofluoromethane, sealed in a Rotaflo-tapped Pyrex ampoule (15 ml), were maintained at room temperature for 4 days in diffuse daylight. Unchanged bromine was removed with mercury, and the residue was fractionated *in vacuo* to give trichlorofluoromethane, unchanged hexadiene (0.011 g, 0.04 mmol, 1%), and a 7 : 1 mixture of *endo*-5,*exo*-6- and *cis*,*exo*-5,6-dibromo-derivatives (0.893 g, 2.00 mmol, 73%) (Found: C, 21.8; F, 42.9. Calc. for $C_8Br_2F_{10}$: C, 21.5; F, 42.5%), condensing at −45 °C. A trace of orange-brown oil remained in the tube.

The dibromides were separated by g.l.c. (10 m SE30 at 136 °C) to give, in order of increasing retention time, endo-5,exo-6-*dibromo*-1,3,5,6-*tetrafluoro*-2,4-*bis*(*trifluoromethyl*)-*bicyclo*[2.2.0]*hex*-2-*ene* (0.700 g, 1.57 mmol, 57%) (Found: C, 21.7; F, 42.4%), $\nu_{max.}$ 1 738vs, sh and 1 732vs cm^{-1} (CF=C·CF_3 str.), as a liquid, b.p. 139—140 °C at 755 mmHg (Siwoloboff), and cis,exo-5,6-*dibromo*-1,3,5,6-*tetrafluoro*-2,4-*bis*(*trifluoromethyl*)*bicyclo*[2.2.0]*hex*-2-*ene* (0.051 g, 0.11 mmol, 4%), $\nu_{max.}$ 1 736vs, sh and 1 732vs cm^{-1} (CF=C·CF_3 str.).

The ^{19}F n.m.r. spectrum of the *endo*,*exo*-dibromide showed absorption at −14.8 (F-2, $J_{2,3}$ 8.7, $J_{2,6}$ 7.7, $J_{1,2}$ 0.8 Hz), −13.5 (F-4, $J_{4,5}$ 12.2, $J_{1,4}$ 4.6, $J_{4,6}$ 1.2 Hz), +2.5 (F-3), 13.4 (F-6), 26.4 (F-5), and 91.0 p.p.m. (F-1). That of the *cis*,*exo*-dibromide (12% solution in its isomer) showed bands at −14.9 (F-2), −12.9 (F-4), +1.1 (F-3), 28.0 (F-6), 35.0 (F-5), and 91.3 p.p.m.

(iii) *Reaction with sodium methoxide*. The hexadiene (1.065 g, 3.73 mmol), sodium methoxide (0.126 g, 2.96 mmol), and diethyl ether (1.131 g), sealed in a Rotaflo-tapped Pyrex ampoule (15 ml), were maintained at room temperature for 4 days. Fractionation of the volatile material *in vacuo* gave diethyl ether, unchanged hexadiene (0.160 g, 0.56 mmol, 15%), condensing at −78 °C, and a 1 : 4 mixture (0.663 g) of unchanged hexadiene and its methoxy-derivative, condensing at −45 °C. The last fraction was separated by g.l.c. (2 m SE30 at 60 °C) to give recovered hexadiene (0.096 g, 0.35 mmol, 9%), and 1,2,3-*trifluoro*-5-*methoxy*-4,6-*bis*(*trifluoromethyl*)*bicyclo*[2.2.0]*hexa*-2,5-*diene* (0.400 g, 1.34 mmol, 40% yield based upon hexadiene converted) (Found: C, 36.4; H, 1.2%; *M*, 298. $C_9H_3F_9O$ requires C, 36.2; H, 1.0%; *M*, 298), $\nu_{max.}$ 1 767s (CF=CF str.) and 1 685vs cm^{-1} (MeO·C=C·CF_3 str.), as a liquid, b.p. 85—90 °C at 755 mmHg (Siwoloboff); τ 5.84(s); ^{19}F bands at −18.7 (F-6), −9.5 (F-4), +45.3 (F-2), 49.4 (F-3), and 115.0 p.p.m. (F-1). When heated at 140 °C for 15 h, the methoxy-hexadiene was quantitatively converted into 1,2,3-*trifluoro*-5-*methoxy*-4,6-*bis*(*trifluoromethyl*)*benzene* (Found: C, 36.5; H, 1.1; F, 57.0%; *M*, 298. $C_9H_3F_9O$ requires C, 36.2; H, 1.0; F, 57.4%; *M*, 298), as a liquid, b.p. 152.5—154.5 °C at 756 mmHg (Siwoloboff); τ 6.21(s); ^{19}F bands at −19.6 (F-4 and -6, $[X_3]_2$ part of an $[AX_3]_2$ system, analysis [17] of which yielded $J_{1,6}$ 26.9, $J_{1,3}$ 15.2, and $J_{1,4}$ 1.7 Hz), +50.4 (F-1 and -3), and 86.1 p.p.m. (F-2, $J_{1,2}$ 19.6 Hz).

Characterisation of the para-*Bonded Benzenes*.—The work described above required the identification of perfluorodimethylbicyclo[2.2.0]hexa-2,5-dienes, where there are six possible isomers (see Scheme 3). The following observations are pertinent to this. Thermal aromatisation of polyfluoro-*para*-bonded benzenes occurs by cleavage of the 1,4-carbon–carbon bond, not by some more complex skeletal rearrangement, and a number of unequivocal examples are known.[1,4,5] The groupings FC:CF and FC:C·CF_3 are readily distinguished by i.r. spectroscopy, showing stretching frequencies in the ranges 1 772—1 777 and 1 714—1 736

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* Numbering corresponds to the compound's systematic name; coupling constants not quoted were not determined because of spectral intensity and/or complexity.

[17] P. Diehl, R. K. Harris, and R. G. Jones, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 45.

cm^{-1}, respectively.[1,4] The two observations alone will largely distinguish a particular hexadiene. Apart from confirming the molecular formula, mass spectrometry is not particularly useful, but the hexadienes show characteristic and distinct ^{19}F n.m.r. spectra. For the compounds studied here and earlier,[1,5,7] the following generalisations may be made: (i) olefinic CF_3 groups absorb in the range -14.0 to -11.3 p.p.m. and they have a regular effect on the chemical shifts of the remaining fluorines; (ii) olefinic fluorines of the type $F_3C{\cdot}C{:}C\mathit{F}$ absorb in the range 4.2—9.8 p.p.m. and of the type FC:CF in the range 41.9—49.2 p.p.m.; (iii) the magnitudes of the coupling constants, where determined, fall into the pattern previously established;[5,7] and (iv) the symmetry of some isomers limits the number of distinct fluorines. Substitution by methoxide on isomer (II), the subsequent thermal aromatisation of the methoxy-product, and cycloaddition[18] to isomers (II) and (X), occur as expected.

In the light of these criteria the identification of isomer (II) is firm, that of isomer (X) would only remain in doubt if the n.m.r. and i.r. data were taken in complete isolation, that of isomer (IV) rests particularly on its thermal isomerisation and on the number and chemical shifts of the absorptions in its ^{19}F n.m.r. spectrum, that of isomer (XII) rests somewhat tentatively on its partial n.m.r. spectrum and its isomerisation to perfluoro-*m*-xylene, and that of isomer (VIII) more tentatively on its showing ^{19}F n.m.r. absorptions for $F_3C{\cdot}C{:}C$ and FC:CF nuclei of approximately the correct intensity. No evidence was found for the presence of the remaining *para*-bonded benzene (VI).

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[18] Part VIII, M. G. Barlow, G. M. Harrison, R. N. Haszeldine, R. Hubbard, M. J. Kershaw, and D. R. Woodward, following paper.