

Valence-bond Isomer Chemistry. Part VI.¹ Photochemical Interconversion of Perfluoro-1,3,5- and -1,2,4-trimethylbenzenes via *para*-Bonded Benzene and Prismane Isomers

By Michael G. Barlow, Robert N. Haszeldine,* and Melvyn J. Kershaw, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Upon u.v. irradiation in the vapour phase, perfluoro-1,3,5-trimethylbenzene is reversibly isomerized to perfluoro-1,2,4-trimethylbenzene, via the valence-bond isomers, perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene, -1,3,5-trimethyltetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane, and -1,2,5-trimethylbicyclo[2.2.0]hexa-2,5-diene. The physical properties of the valence-bond isomers are discussed. Perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene undergoes photochemical addition of 1 mol. equiv. of bromine, and substitution of an olefinic fluorine atom by methoxide.

PHOTOCHEMICAL isomerizations of aromatic compounds are well known, but the intermediates, usually presumed to be valence-bond isomers (*para*-bonded benzenes, prismanes, and benzvalenes), have for the most part proved elusive. The xylenes are interconvertible by u.v. irradiation, both in the liquid and the vapour phase,²⁻⁵ and the predominance of 1,2-methyl shifts has led to the suggestion of benzvalene intermediates, although *para*-bonded benzenes and prismanes may be involved, particularly in reactions brought about by vacuum u.v. light.⁶ The conversion of 1,3,5- into 1,2,4-trimethylbenzene has been shown by ¹⁴C labelling to involve transposition of ring atoms, possibly through benzvalene intermediates.⁷ Only in the case of the interconversion of 1,3,5- and 1,2,4-tri-*t*-butylbenzenes have such benzvalenes been characterised,⁸ and the

alternative *para*-bonded benzene and prismane route has not been unequivocally demonstrated, although it has been invoked in the photochemical conversion of 1,2,4,5-tetra-*t*-butylbenzene into 1,2,3,5-tetra-*t*-butylbicyclo[2.2.0]hexa-2,5-diene and 1,2,3,5-tetra-*t*-butylbenzene.⁹ In the heterocyclic field, prismane intermediates have been suggested for the isomerizations of picolines and lutidines,¹⁰ and *para*-bonded isomers have been shown to be possible intermediates in the isomerization of certain fluorinated pyridazines to pyrazines.¹¹

Introduction of fluoro-substituents, and particularly of perfluoroalkyl groups, leads to a notable increase in both stability and ease of formation of valence-bond isomers of aromatic compounds. The valence-bond isomers of hexakis(trifluoromethyl)benzene comprise the most complete such system known,¹² and they owe their thermal stability at least in part to destabilization of the

¹ Part V, M. G. Barlow, R. N. Haszeldine, W. D. Morton, and D. R. Woodward, *J.C.S. Perkin I*, 1973, 1798.

² K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1964, **86**, 2307.

³ R. B. Cundall and A. J. R. Voss, *Chem. Comm.*, 1968, 903; 1969, 116.

⁴ D. Anderson, *J. Phys. Chem.*, 1970, **74**, 1687.

⁵ W. A. Noyes and D. A. Harter, *J. Phys. Chem.*, 1971, **75**, 2741.

⁶ H. R. Ward, *J. Amer. Chem. Soc.*, 1967, **89**, 2367.

⁷ L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. Yang, *J. Amer. Chem. Soc.*, 1966, **87**, 675.

⁸ I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1968, **90**, 5868.

⁹ E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 1964, 3803.

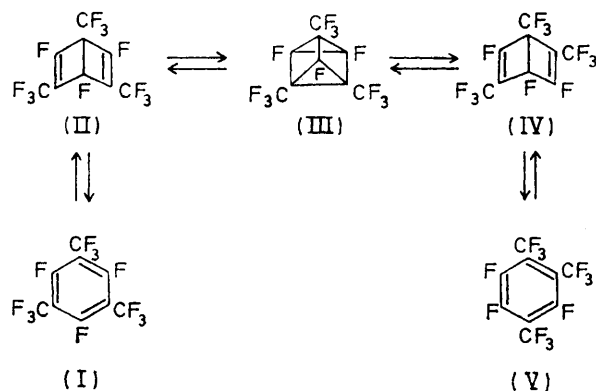
¹⁰ S. Caplain and A. Lablache-Combier, *Chem. Comm.*, 1970, 1247.

¹¹ R. D. Chambers, W. K. R. Musgrave, and K. C. Srivastava, *Chem. Comm.*, 1971, 264; D. W. Johnson, V. Austel, R. S. Field, and D. M. Lemal, *J. Amer. Chem. Soc.*, 1970, **92**, 7505.

¹² M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc. (C)*, 1970, 1232 (includes references to earlier work).

ground state aromatic compound by non-bonding interactions between bulky trifluoromethyl groups.¹³ We have studied perfluoro-1,3,5-trimethylbenzene, since any valence-bond isomers are expected to show enhanced stability compared with their hydrocarbon counterparts, and the effective ring symmetry (D_{3h}) limits the number of possible isomers.

Perfluoro-1,3,5-trimethylbenzene (I) was prepared (60%) by the reductive defluorination of perfluoro-1,3,5-trimethylcyclohexane over tri-iron tetraoxide at 475–490 °C. Also formed were small amounts (4%) of perfluoro-1,2,4-trimethylbenzene, possibly arising, at least



SCHEME 1

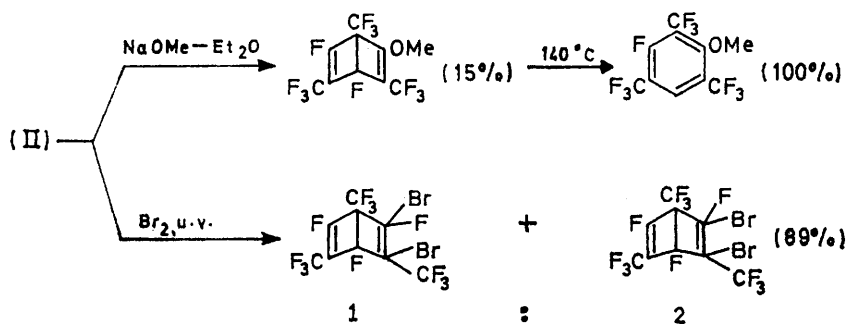
in part, from small amounts of 1,2,4-isomer in the starting material.

U.v. irradiation of perfluoro-1,3,5-trimethylbenzene in the vapour phase gave perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene (II), -1,3,5-trimethyltetra-cyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (III), -1,2,5-trimethylbicyclo[2.2.0]hexa-2,5-diene (IV), and -1,2,4-trimethylbenzene

u.v. light used; and (iii) the diluent gas. The results indicated that at $\lambda > 230$ nm, only the *para*-bonded isomer (II) is formed initially; subsequently the prismane (III) is formed, along with the *para*-bonded isomer (IV), and the benzene (V) is only produced in trace amounts by long-term irradiation. The effect of change in wavelength of light used was investigated in a preliminary fashion by use of various glass filters. In general, there was an increase in conversion of compound (I) at shorter wavelengths, and an increase in yield of isomers (III)–(V). At the shortest wavelengths used (>200 nm), the conversion of compound (I) fell off, and greater amounts of compound (V) were formed, probably as a result of increased absorption by the *para*-bonded isomers (II) and (IV). The presence of argon, an inefficient acceptor of vibrational excitation,¹⁴ as diluent gas reduced the conversion to non-isomeric products. High pressures of air did not suppress the formation of the isomer (II), but did that of the subsequently formed isomers. In the liquid phase, isomerization was almost completely suppressed and only the hexadiene (II) (1–3%) was formed. The hexadienes formed the prismane (III) in the liquid phase, but rearomatization was favoured, particularly for the hexadiene (II). In none of the foregoing irradiations was the formation of benzvalene isomers detected.

These results are consistent with initial formation of the hexadiene (II), in a process requiring some vibrational excitation, subsequent formation of the prismane (III), with simultaneous and subsequent formation of the hexadiene (IV), formation of either hexadiene being reversible at shorter wavelengths.

Both hexadienes are liquids comparable in stability to previously reported polyfluorobicyclo[2.2.0]hexa-2,5-dienes,¹⁵ but the prismane is far less stable, with a half-life



SCHEME 2

(V). Similarly, irradiation of compound (V) gave the isomers (II)–(IV). Apart from some fragmentation and polymerization, particularly in the early stages, the reaction was clean and gave up to 92% yield of isomers, and up to 80% of compound (I) was converted. The effects of the following factors were investigated in a qualitative fashion for the isomerization of compound (I): (i) the time of irradiation; (ii) the wavelength of

in solution towards reversion to the hexadienes (II) and (IV), in the ratio 1 : 6, of 19 h at 35 °C. Its isomerization appears to be readily catalysed by glass and other surfaces, and it has so far escaped isolation.

The hexadiene (II) undergoes the expected reactions,^{15,16} undergoing substitution by methoxide ion, and

¹⁴ T. L. Cottrell and J. C. McCoubrey, 'Molecular Energy Transfer in Gases,' Butterworths, London, 1961.

¹⁵ C. Camaggi and F. Gozzo, *J. Chem. Soc. (C)*, 1969, 489.

¹⁶ M. G. Barlow, R. N. Haszeldine, W. D. Morton, and D. R. Woodward, *J.C.S. Perkin I*, 1972, 2170.

¹³ D. M. Lemal and L. H. Dunlap, *J. Amer. Chem. Soc.*, 1972, 94, 6562.

slow photochemical addition of bromine (Scheme 2). Both dibromides show a low-field shift of bridgehead fluorine signals in their ^{19}F n.m.r. spectra, indicating an adjacent *exo*-bromine atom,¹⁶ and if the previous assignments of 5,6-dibromohexafluorobicyclo[2.2.0]hex-2-enes are correct, and allowance is made for the presence of CF_3 groups, then the most prevalent is the *trans*-isomer, which shows substantial coupling (J 12.8 Hz) of bridgehead CF_3 group and adjacent CFBr group fluorine nuclei.

Russian workers have reported recently that perfluoro-1,3,5-trimethylbenzene is photoisomerized only to the hexadiene (II).¹⁷ However, their conditions (low-pressure mercury lamp and a flow system) are expected to favour this isomerisation only.

The photochemical isomerization of perfluoro-1,3,5- to -1,2,4-trimethylbenzene represents the first unequivocal example of such a change which occurs *via para*-bonded and prismane isomers. The stabilising effect of fluoro- and perfluoroalkyl substituents upon highly strained compounds is again apparent.

EXPERIMENTAL

Experimental techniques were similar to those described previously.¹ Photochemical reactions were, for the most part, carried out in the vapour phase in a reactor (5 l) consisting of a Pyrex vessel fitted with a central water-cooled, quartz immersion well, which carried a medium-pressure mercury lamp (Hanovia U.V.S. 500). The lamp was surrounded, where appropriate, by a filter (nominal cut-off wavelength) of Vycor 7910 (230 nm), Correx 9700 (255 nm), or 1 mm Pyrex (270 nm) glass. G.l.c. analyses and separations were carried out using a 7 m TXP column, with nitrogen as carrier gas.

Preparation of Perfluoro-1,3,5- and -1,2,4-trimethylbenzenes.

—Perfluoro-1,3,5-trimethylcyclohexane* (30.64 g, 68.1 mmol) was passed in a stream of dry nitrogen (30 ml min⁻¹) over tri-iron tetraoxide pellets [350 g of cylindrical pellets (6 mm × 6 mm), total volume *ca.* 175 ml], contained in a mild steel tube (70 cm × 19 mm i.d., empty volume *ca.* 220 ml), at 475–490 °C at a rate of *ca.* 1 g h⁻¹ (contact time *ca.* 0.6 min), to give a mixture shown by g.l.c. (at 130 °C) to consist of the unchanged cyclohexane (10.91 g, 24.3 mmol, 36% recovery, shown to contain some unsaturated material by ^{19}F n.m.r. spectroscopy); perfluoro-1,3,5-trimethylbenzene (I) (8.84 g, 27.3 mmol, 62% yield based upon cyclohexane converted), λ_{max} (hexane) 205 (ϵ 7600) and 255 (200), λ_{min} 232 nm (70); and perfluoro-1,2,4-trimethylbenzene (V) (0.57 g, 1.7 mmol, 4%), λ_{max} 211 (ϵ 6100) and 284 (2770), λ_{min} 238 (90). The product of several such runs was distilled (Nester–Faust 36 in spinning band) and the aromatic fraction, b.p. 136–140 °C, was separated by g.l.c. to give perfluoro-1,3,5-trimethylbenzene (Found: C, 32.0%; M , 336. Calc. for C_9F_{12} : C, 32.2%; M , 336), b.p. 136–137 °C at 757 mmHg (lit.,¹⁸ 137–138 °C), and perfluoro-1,2,4-trimethylbenzene (Found: C, 32.1%; M , 336. C_9F_{12} requires C, 32.2%; M , 336), b.p. 142.5–143.5 °C at 755 mmHg (Siwoloboff).

The iron oxide pellets were periodically regenerated by the passage of steam at 500 °C.

* ^{19}F N.m.r. spectroscopy indicated this to be largely (>90%) a 2 : 1 mixture of *cis*, *cis*- and *cis*, *trans*-isomers.

† For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

The Perfluorotrimethylbenzene Valence-bond Isomer System.

—(a) *Vapour phase u.v. irradiation of perfluoro-1,3,5-trimethylbenzene (I).* Argon (50 mmHg) and perfluoro-1,3,5-trimethylbenzene (1.333 g, 3.96 mmol), contained in the photochemical reactor, were irradiated ($\lambda > 230$ nm) for 45 h. The volatile products were removed and fractionated *in vacuo* to give: (i) a mixture of silica tetrafluoride (0.083 g, 0.08 mmol) and carbonyl fluoride (0.020 g, 0.30 mmol), condensing at –196 °C; (ii) a mixture, shown by ^{19}F n.m.r. and i.r. spectroscopy and g.l.c. to consist of perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene [0.883 g, 2.63 mmol, 85% yield based on compound (I) converted], perfluoro-1,3,5-trimethyltetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (0.014 g, 0.04 mmol, 1%), and perfluoro-1,2,5-trimethylbicyclo[2.2.0]hexa-2,5-diene (0.070 g, 0.20 mmol, 7%), condensing at –78 °C; and (iii) a mixture of perfluoro-1,3,5-trimethylbenzene (0.294 g, 0.88 mmol, 22% recovery) and perfluoro-1,2,4-trimethylbenzene (0.003 g, 0.009 mmol, 0.3%), condensing at –36 and –45 °C. Traces of brown, viscous, polymeric material remained in the reactor.

Appropriate fractions from several such irradiations were separated by g.l.c. (at 125 °C for the benzene, and at 40 °C for the hexadienes) to give the two benzenes, and, in order of increasing retention time: (i) perfluoro-1,2,5-trimethylbicyclo[2.2.0]hexa-2,5-diene (IV) (Found: C, 31.9%; M , 336. C_9F_{12} requires C, 32.2%; M , 336), ν_{max} 1736s, sh and 1730vs cm⁻¹ ($\text{CF}=\text{C}-\text{CF}_3$ str.), λ_{max} (vapour) 201 nm (490), as a liquid, b.p. 76.8 °C; and (ii) perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene (II) (Found: C, 32.0%; M , 336), ν_{max} 1735vs cm⁻¹ ($\text{CF}=\text{C}-\text{CF}_3$ str.), λ_{max} 202 nm (2300), as a liquid, b.p. 74.5 °C.

Many similar photoisomerizations were carried out with variations in the time of irradiation, the wavelength of light used, and the concentration of diluent gas. Some of these are summarized in the Table.

Long-term irradiation of the liquid benzene, or of its solutions in perfluoro-*n*-pentane or perfluorodiethyl ether, produced only trace amounts (1–3%) of perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene. No isomerization was observed when the benzene was passed through a packed silica tube heated to 600°.

(b) *Irradiation of perfluoro-1,2,4-trimethylbenzene (V).* Argon (50 mmHg) and perfluoro-1,2,4-trimethylbenzene (0.712 g, 2.12 mmol) were irradiated ($\lambda > 230$ nm) for 41 h to give perfluoro-1,2,4-trimethylbenzene (0.065 g, 0.19 mmol, 9% recovery), perfluoro-1,2,5-trimethylbicyclo[2.2.0]hexa-2,5-diene [0.481 g, 1.43 mmol, 74% yield based on compound (V) converted], perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene (0.049 g, 0.15 mmol, 8% yield), and perfluoro-1,3,5-trimethyltetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (0.061 g, 0.18 mmol, 9% yield).

Properties of the Perfluorotrimethylbenzene Valence-bond Isomers.—Mass spectral data for the two benzenes and the two bicyclohexadienes are available as Supplementary Publication No. SUP 20994 (3 pp.).† The partial fragmentation pattern shown in Scheme 3 was established from the presence of metastable ions for all four isomers, except that paths to C_7F_7^+ were not observed for the benzene (I), and to $\text{C}_7\text{F}_6^{++}$ for the hexadiene (IV). In all cases the parent ion was prominent and $\text{C}_9\text{F}_{11}^+$ provided the base peak for all

¹⁷ V. V. Brovko, T. D. Petrova, A. K. Petrov, V. A. Sokolenko, G. G. Yakobson, and L. I. Kann, *Izvest. sibirsk. Otdel. Akad. Nauk S.S.S.R., Ser. Khim. Nauk*, 1971, 2, 103.

¹⁸ V. E. Platonov, V. N. Ermolenko, G. G. Yakobson, and N. N. Vorzhtsov, *Bull. Acad. Sci., U.S.S.R.*, 1968, 2, 2606.

except the hexadiene (IV), where $C_8F_9^+$ was the base peak; this last ion was also more prominent for the benzene (IV) than for the remaining compounds and the CF_3^+ ion was also more prominent for the two compounds with adjacent CF_3 groups.

(a) *Perfluoro-1,3,5-trimethylbicyclo[2.2.0]hexa-2,5-diene* (II). The vapour pressure of the hexadiene (II), measured over the range 20–60 °C, is given by the equation: $\log_{10}(p/\text{mmHg}) = 8.45 - 1940/T$, whence the calculated b.p. is

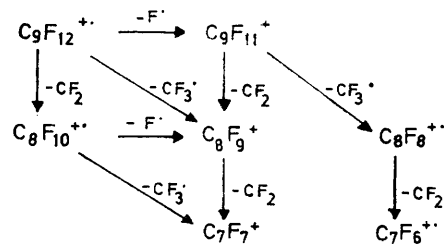
in vacuo to yield trichlorofluoromethane, the unchanged hexadiene (0.377 g, 1.12 mmol, 46% recovery), perfluoro-1,3,5-trimethylbenzene (0.027 g, 0.08 mmol, 5% yield based on hexadiene converted), and an inseparable 2:1 mixture (0.606 g, 1.23 mmol, 89%) of *endo-5,exo-6-* and *exo-5,exo-6-* dibromo-1,3,5-trifluoro-2,4,6-tris(trifluoromethyl)bicyclo[2.2.0]hex-2-enes (Found: C, 21.5; F, 45.3. Calc. for $C_9Br_2F_{12}$: C, 21.8; F, 46.0%), ν_{max} , 1741 vs, sh and 1737 vs cm^{-1} ($CF=C-F_3$ str), as a liquid, b.p. 153–155 °C at 754

Vapour phase photochemical isomerizations of perfluoro-1,3,5-trimethylbenzene (I)

Wavelength (nm)	Time (h)	Diluent gas (mmHg)	Perfluoro-1,3,5- trimethylbenzene		Conversion (g) (%)	Product (%) ^a			
			taken (g, mmol)	recovered (g, mmol)		(II)	(III)	(IV)	(V)
> 255	47.0	Ar (50)	6.04, 17.20	4.95, 14.71	1.09 (18)	54	5	25	< 0.1
> 230	48.0	Ar (50)	4.90, 14.60	3.59, 10.07	1.31 (27)	57	14	11	< 0.1
> 270	200	Ar (50)	4.12, 12.28	4.02, 11.95	0.10 (2)	42 ^b		20 ^b	
< 230	1.0	Ar (50)	1.00, 3.10	0.79, 2.36	0.21 (21)	31			
< 230	3.0 ^c	Ar (50)	1.00, 3.10	0.66, 1.97	0.34 (34)	48	< 0.2		
> 230	6.0 ^d	Ar (50)	1.00, 3.10	0.62, 1.85	0.38 (38)	66	< 0.5		
> 230	18.5	Ar (50)	0.91, 2.70	0.21, 0.62	0.70 (77)	83	3	4	
> 230	45.0	Ar (50)	1.33, 3.97	0.29, 0.88	1.04 (78)	85	1	7	< 0.1
> 200	47.8	Ar (50)	4.91, 14.61	3.96, 11.80	0.95 (19)	25	12	11	41
> 200	41.5	Air (500)	2.19, 6.52	0.43, 1.44	1.76 (81)	61	2	8	1
> 200	42.0		2.00, 5.95	1.07, 3.18	0.93 (53)	18	17	27	20

^a Product composition determined by ^{19}F n.m.r. spectroscopic analysis of the total product. ^b By i.r. spectroscopy. ^c Product mixture after 1 h reconstituted and irradiated for 2 h. ^d Product mixture after 3 h reconstituted and irradiated for 3 h.

74.5 °C, the latent heat of vaporization is 8860 cal mol^{-1} , and Trouton's constant is 25.5 cal $\text{deg}^{-1} \text{mol}^{-1}$. It shows ^{19}F n.m.r. bands (neat liq., numbering corresponds to



SCHEME 3

systematic name) at -11.4 (F-3,5, $[X_3]_2$ part of an $[AX_3]_2$ system with $|J_{2,3} + J_{3,6}|$ 9.8 Hz), -9.7 (F-1, dt, $J_{1,4}$ 6.9, $J_{1,2}$ 0.5 Hz), 8.0 (F-2,6, complex), and 118.0 p.p.m. (F-4, sextet, $J_{1,4}$ $J_{2,4}$ 6.8 Hz). Its half-life, in hexafluorobenzene solution, towards aromatization to perfluoro-1,3,5-trimethylbenzene, is 5.4 ± 0.1 h at 90 °C.

(i) *U.v. irradiation*. The hexadiene (II) (0.063 g, 0.188 mmol) and perfluoro-*n*-pentane (0.412 g), 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 conversion into the benzene (I) and the prismane (III) in the ratio 25:1. After 50 h irradiation, when the mixture contained the maximum (3%) of prismane, the hexadiene (IV) was just detectable ($<1\%$).

(ii) *Bromination*. The hexadiene (0.817 g, 2.43 mmol), bromine (0.555 g, 3.46 mmol), and trichlorofluoromethane (0.989 g), sealed in a silica ampoule (15 ml), were maintained at room temperature in diffuse daylight (52 h); no loss of bromine colour was apparent. The mixture was then irradiated with u.v. light (89 h), bromine was removed by shaking with mercury, and the product was fractionated

mmHg (Siwoloboff), which was purified by g.l.c. (at 150 °C). Traces of a dark red oil (0.050 g) remained in the ampoule.

The ^{19}F n.m.r. spectrum of the liquid mixture showed bands assigned to the *trans*-isomer at -15.8 (F-2), -14.0 (F-4), -9.9 (F-6), $+6.6$ (F-3), 17.2 (F-5), and 86.0 p.p.m. (F-1), and to the *cis*-isomer at -15.8 (F-2), -13.2 (F-4), -10.2 (F-6), $+4.3$ (F-3), 28.8 (F-5), and 87.3 p.p.m. (F-1).

(iii) *Reaction with sodium methoxide*. Hexadiene (0.965 g, 2.87 mmol), sodium methoxide (0.128 g, 2.30 mmol), and diethyl ether (5 ml), sealed in a Rotaflo-tapped Pyrex ampoule (15 ml), were maintained at -78° for 1 h and at room temperature for 20 h. Fractionation of the volatile material *in vacuo* gave a mixture (0.716 g) containing the unchanged hexadiene (85%). This mixture was sealed up with fresh sodium methoxide (0.097 g, 1.1 mmol) and diethyl ether (1 ml). After 9 days at room temperature the volatile product was fractionated *in vacuo* to give diethyl ether, the unchanged hexadiene (0.108 g, 0.32 mmol, 11% recovery), condensing at -78°C , and a mixture (0.397 g), condensing at -36°C , shown by ^{19}F n.m.r. spectroscopy to comprise the unchanged hexadiene (4%), methoxy-substituted hexadiene (88%), and probably dimethoxy-hexadiene (8%). This mixture was separated by g.l.c. to give the unchanged hexadiene (0.013 g) and 1,3-difluoro-5-methoxy-2,4,6-tris(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene (0.132 g, 0.38 mmol, 15%) (Found: C, 34.5; H, 0.9%; M, 348. $C_{10}H_3F_{11}O$ requires C, 34.5; H, 1.0%; M, 348), ν_{max} , 1728s ($CF=C-F_3$ str.), 1687s, sh, and 1682s cm^{-1} ($MeO-C=C-F_3$ str.), as a liquid, b.p. 90–94 °C at 755 mmHg (Siwoloboff). Remaining in the ampoule was an orange solid, partially soluble in water (positive tests for Na^+ and F^-), leaving a dark-brown liquid, which gave a complex but ill-defined i.r. spectrum, with bands indicative of the presence of the $CF_2C=CF_3$ grouping; it was not examined further.

The methoxy-hexadiene showed τ 5.80 (s) and δ_F -18.8 (F-6), -12.0 (F-2, $J_{2,3}$ 9.7 Hz), -9.8 (F-4, $J_{1,4}$ 6.9, $J_{3,4}$ 0.9 Hz), $+9.1$ (F-3, $J_{2,3}$ 9.7 Hz), and 113.8 p.p.m. (F-1). When

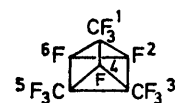
heated at 140 °C for 10 h, the methoxy-hexadiene was quantitatively converted into 1,3-difluoro-5-methoxy-2,4,6-tris(trifluoromethyl)benzene (Found: C, 34.5; H, 0.9%; *M*, 348. $C_{10}H_3F_{11}O$ requires C, 34.5; H, 1.0%; *M*, 348), as a liquid, b.p. 140–142 °C at 760 mmHg (Siwoloboff), τ 6.19 (s), δ_F –20.0 (F-2, $J_{1,2}$ 9.5 Hz), –19.7 (F-4,6, $[X_3]_2$ part of an $[AX_3]_2$ system, analysis¹⁹ of which yielded $J_{3,4}$ 28.5, $J_{1,3}$ 9.5, and $J_{1,4}$ 1.1 Hz), and +25.2 p.p.m. (F-1,3).

(b) *Perfluoro-1,2,5-trimethylbicyclo[2.2.0]hexa-2,5-diene* (IV). The vapour pressure of the hexadiene (IV), measured over the range 20–60 °C, is given by the equation: $\log_{10}(p/\text{mmHg}) = 7.33 - 1560/T$, whence the calculated b.p. is 76.8 °C, the latent heat of vaporization is 7140 cal mol^{–1}, and Trouton's constant is 20.4 cal deg^{–1} mol^{–1}. It shows ¹⁹F n.m.r. bands at –11.9 (F-5, $J_{5,6}$ 9.0, $J_{4,5}$ 0.3 Hz), –11.7 (F-2, $J_{2,3}$ 9.8, $J_{1,2} = J_{2,4}$ 1.8 Hz), –9.0 (F-1, $J_{1,4}$ 7.0, $J_{1,3}$ 2.6, $J_{1,6}$ 0.8 Hz), +4.2 (F-3 or 6), 6.8 (F-6 or 3), and 117.1 p.p.m. (F-4). Its half-life, in hexafluorobenzene solution, towards aromatization to perfluoro-1,2,4-trimethylbenzene is 14.1 ± 0.2 h at 90 °C.

(i) *U.v. irradiation*. The hexadiene (IV) (0.052 g, 0.155 mmol) and perfluoro-*n*-pentane (0.456 g), sealed in a silica n.m.r. tube, were irradiated (>200 nm) at 20 cm from the lamp, and periodically examined by ¹⁹F n.m.r. spectroscopy, which indicated initial conversion into the benzene (V) and the prismane (III), in approximately equal amounts. The proportion of prismane passed through a maximum (24%) after 25 h irradiation, and long-term irradiation led mainly to the benzene (V).

(c) *Perfluoro-1,3,5-trimethyltetracyclo[2.2.0.0.2^a.0.3^b.5]hexane* (III). The prismane (III) has so far escaped all attempts at isolation, despite its moderate thermal stability in a solution of its hexadiene isomers (half-life 19 ± 1 h at 35 °C). A

mixture of the hexadienes (II) (52%) and (IV) (24%) and the prismane (23%), upon attempted g.l.c. separation (20 °C), showed only two peaks corresponding in retention times to two hexadienes, and when the total eluant from the column was collected, it was shown by ¹⁹F n.m.r. spectroscopy to comprise the hexadienes (II) and (IV) in the ratio 58:42. When separation of mixtures containing the prismane was attempted by repeated fractional condensation *in vacuo*, then only the hexadienes (II) and (IV) were obtained; the prismane appears to be unstable to prolonged contact with glass surfaces. Its identity is assured upon the following grounds. When heated at 35 °C, it is isomerized quantitatively to the hexadienes (II) and (IV) in the ratio 1:6. It shows ¹⁹F n.m.r. bands (37% solution in a mixture of its hexadiene isomers) at –16.4 (3F, F-1, $J_{1,2}$ 3.6, $J_{1,4}$ 0.9, $J_{1,3} \leq 0.1$ Hz), –15.8 (6F, F-3,5, $J_{3,4}$ 2.8, $|J_{2,3} + J_{3,6}|$ 4.0 Hz), +106.8 (1F, F-4), and 119.0 p.p.m. (2F, F-2,6, $J_{2,4}$ 5.1 Hz). In particular, the chemical shifts of the two high-field



absorptions are characteristic of tertiary fluorines attached to a saturated carbon atom.

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¹⁹ P. Diehl, R. K. Harris, and R. G. Jones, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 45.