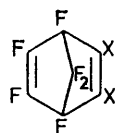


## Polyfluorocyclopentadienes. Part VII.<sup>1</sup> Synthesis of Perfluoronorbornadiene and Perfluoronorbornene from Perfluorocyclopentadiene

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Perfluorocyclopentadiene combines thermally with bis(trimethylstannyl)acetylene to yield a Diels–Alder adduct, 1,2,3,4,7,7-hexafluoro-5,6-bis(trimethylstannyl)bicyclo[2,2,1]hepta-2,5-diene (1). Cleavage of the C–Sn bonds in this adduct with hydrogen chloride to give 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene and with chlorine, bromine, or iodine to give 2,3-dihalogenohexafluorobicyclo[2,2,1]hepta-2,5-dienes proceeds smoothly to give excellent yields of the expected bicycloheptadienes, in contrast to cleavage with fluorine. The chlorinolysis product, 2,3-dichloro-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene (2) reacts with cobalt trifluoride to give 2,3-dichloro-1,2,3,4,5,5,6,6,7,7-decafluorobicyclo[2,2,1]heptane; zinc-dechlorination of the last product provides perfluorobicyclo[2,2,1]hept-2-ene (perfluoronorbornene) and 2-chloro-1,3,4,5,5,6,6,7,7-nonafluorobicyclo[2,2,1]hept-2-ene. Photochemical chlorination of the dichlorohexafluorodiene (2) gives a mixture of 5,5,6,6-tetrachloro-1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene and 2,3,5,6-tetrachloro-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hept-2-ene; fluorination with cobalt trifluoride of this mixture followed by zinc-dechlorination of the isomeric tetrachloro-octafluorobicyclo[2,2,1]heptanes thus obtained yields perfluorobicyclo[2,2,1]hepta-2,5-diene (perfluoronorbornadiene) and 2-chloro-1,3,4,5,6,7,7-heptafluorobicyclo[2,2,1]hepta-2,5-diene.

PERFLUOROCYCLOPENTADIENE combines with bis(trimethylstannyl)acetylene at room temperature to give 89% yield of a 1 : 1 adduct, shown by <sup>19</sup>F n.m.r. spectroscopy<sup>2</sup> to be of the Diels–Alder type (1); this reaction parallels that between the acetylene and perchlorocyclopentadiene.<sup>3</sup> Like its chloro-analogue,<sup>3</sup> adduct (1) suffers electrophilic cleavage of the tin–carbon bonds when treated with chlorine, bromine, or hydrogen chloride, and high yields of bicyclo[2,2,1]hepta-2,5-dienes (2) (84.5%), (3) (99%), and (4) (90%); also obtainable directly from perfluorocyclopentadiene and acetylene<sup>2</sup>) result. Similarly, cleavage of the adduct (1) with iodine gives the di-iodo-compound (5) (99%), but cleavage with fluorine has so far given perfluoronorbornadiene (6) in only low yield (<5%) together with complex higher-boiling material.

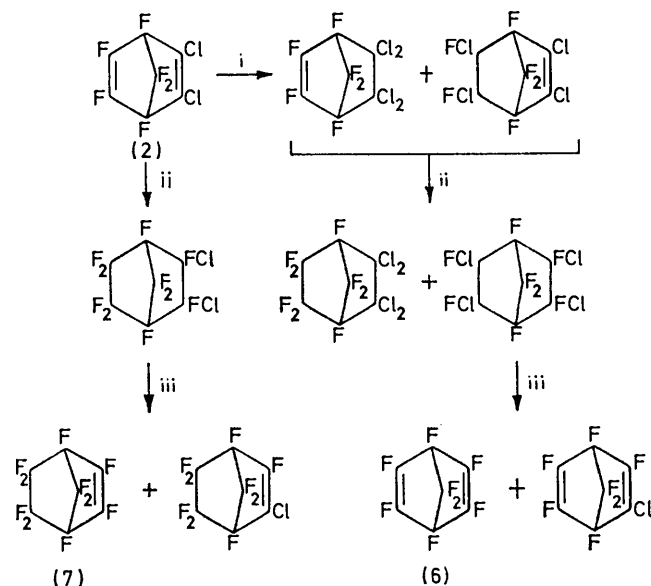


(1) X = Me<sub>3</sub>Sn (4) X = H

(2) X = Cl (5) X = I

(3) X = Br (6) X = F

of its new analogues (2), (3), (5), and (6) are in progress, and the results will be reported later.<sup>5</sup>



SCHEME Reagents: i, Cl<sub>2</sub>, light; ii, CoF<sub>3</sub>, 70–75 °C; iii, Zn dust, boiling (MeO·[CH<sub>2</sub>]<sub>2</sub>)<sub>2</sub>O

2,3-Dichlorohexafluorobicyclo[2,2,1]hepta-2,5-diene (2) can be converted into perfluoronorbornadiene (6) and perfluoronorbornene (7) by the routes shown in the Scheme. The latter fluorocarbon has been separated recently from the complex mixture obtained by pyrolysis of sodium perfluorobicyclo[2,2,1]heptane-1-carboxylate,<sup>4</sup> but the former, a volatile liquid (b.p. 54.4 °C), is new. Studies on the chemistry of the bicycloheptadiene (4) and

<sup>1</sup> Part VI, R. E. Banks, M. Bridge, R. N. Haszeldine, D. W. Roberts, and N. I. Tucker, *J. Chem. Soc. (C)*, 1970, 2531.

<sup>2</sup> See R. E. Banks, A. C. Harrison, R. N. Haszeldine, and K. G. Orrell, *J. Chem. Soc. (C)*, 1967, 1608 for a discussion of the diagnostic n.m.r. parameters.

<sup>3</sup> D. Seyferth and A. B. Evin, *J. Amer. Chem. Soc.*, 1967, **89**, 1468.

<sup>4</sup> S. F. Campbell, J. M. Leach, R. Stephens, and J. C. Tatlow, *J. Fluorine Chem.*, 1971, **1**, 85.

### EXPERIMENTAL

Perfluorocyclopentadiene<sup>6</sup> and bis(trimethylstannyl)acetylene<sup>7</sup> were prepared as described in the literature. Fluorinations with cobalt trifluoride were carried out by use of a reactor comprising a horizontal Pyrex tube (40 × 3 cm) fitted with a B34 cone at the entrance and a vacuum stopcock and B14 cone at the exit, where two product traps and finally a line to a vacuum system could be attached; the central portion (23 cm) of the reactor was wound with a heating tape, which housed a thermometer. The cobalt

<sup>5</sup> R. E. Banks, R. N. Haszeldine, and A. Prodgers, unpublished results.

<sup>6</sup> (a) R. E. Banks, R. N. Haszeldine, and J. B. Walton, *J. Chem. Soc.*, 1963, 5581; (b) R. E. Banks, M. Bridge, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1970, 48.

<sup>7</sup> D. Seyferth, C. Sarafidis, and A. B. Evin, *J. Organometallic Chem.*, 1964, **2**, 417.

trifluoride (*ca.* 25 g) was contained in a copper boat, which was removed at the end of each experiment and placed in a conventional metal reactor for regeneration of the reagent with fluorine at *ca.* 150 °C. The entrance to the Pyrex reactor was closed with a B34 socket carrying a small (10 cm) mercury-filled, closed-end, U-tube manometer and a vacuum stopcock connected to a B14 cone, which allowed the attachment of a reservoir of the chlorofluorobicyclo-compound under investigation. Kel-F grease was used to lubricate stopcocks and joints.

Products were identified by elemental analysis and by i.r. (Perkin-Elmer spectrophotometer model 257), n.m.r. [Perkin-Elmer R10 instrument operating at 60 MHz for <sup>1</sup>H (int. Me<sub>4</sub>Si ref.) and 56.46 MHz for <sup>19</sup>F (ext. CF<sub>3</sub>·CO<sub>2</sub>H ref., positive shifts to high field), or, where stated, a Varian HA-100 instrument operating at 94.1 MHz for <sup>19</sup>F (*p*-CF<sub>3</sub>·S·C<sub>6</sub>H<sub>4</sub>Cl lock signal; the observed shifts were converted to the ext. CF<sub>3</sub>·CO<sub>2</sub>H scale by the subtraction of 35.5 p.p.m.)], and mass (A.E.I. MS902 spectrometer) spectroscopy.

**Reaction of Perfluorocyclopentadiene with Bis(trimethylstannyl)acetylene.**—Perfluorocyclopentadiene (4.96 g, 28.5 mmol) was condensed, *in vacuo*, onto bis(trimethylstannyl)acetylene (10.0 g, 28.5 mmol) contained in a cold (−196 °C) Pyrex ampoule (300 ml), which was sealed and stored at room temperature for 48 h. The involatile product, a yellow oil, was removed from the vessel as a solution in light petroleum (b.p. 30–40 °C; *ca.* 10 ml), which was eluted with the same solvent through a short column of silica gel. The eluate was concentrated to provide white crystals of 1,2,3,4,7,7-hexafluoro-5,6-bis(trimethylstannyl)bicyclo[2,2,1]hepta-2,5-diene (1) (13.3 g, 25.3 mmol, 89%) [Found: C, 30.5; H, 3.5%; *M* (mass spec.), 528 (for <sup>120</sup>Sn). C<sub>13</sub>H<sub>18</sub>F<sub>6</sub>Sn<sub>2</sub> requires C, 29.7; H, 3.4%; *M*, 528 (for <sup>120</sup>Sn)], m.p. 40.5–41 °C, λ<sub>max</sub> (melt) 5.71 μm (CF=CF str.), δ<sub>F</sub> (50% w/w soln. in CCl<sub>4</sub>) +55.0 (CF<sub>2</sub>, AB-type pattern, |J<sub>gem</sub>| 150 Hz, ν<sub>0δ</sub> 1.75 p.p.m.), +78.0 (CF:CF, narrow m), and +116.0 p.p.m. (≥CF, s) (rel. int. 2:2:2), τ (50% w/w soln. in CCl<sub>4</sub>) 9.44 (s, with satellites, J<sub>117Sn-H</sub> 55.5, J<sub>117Sn-H</sub> 58 Hz).

**2,3-Dichloro-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene (2).**—To 1,2,3,4,7,7-hexafluoro-5,6-bis(trimethylstannyl)bicyclo[2,2,1]hepta-2,5-diene (1) (10.6 g, 20.2 mmol) and trichlorofluoromethane (11 g) frozen in a cold (−196 °C) evacuated Pyrex tube (300 ml) was added chlorine (2.84 g, 40.0 mmol); the tube was sealed, *in vacuo*, with a 4 mm PTFE Fischer–Porter needle valve, stored for 1 day at −72 °C, then allowed to warm slowly to room temperature. (CAUTION: This reaction has been carried out on four times the above scale, but once a tremendous explosion occurred when the reaction vessel was removed from a −72 °C bath and momentarily shaken gently.) The volatile product was separated by trap-to-trap fractional condensation at 1–2 mmHg into trichlorofluoromethane (−196 °C trap) and a colourless liquid (−45 °C trap); the latter was passed slowly, *in vacuo*, through a −45 °C trap also containing a cold (−45 °C) finger; trimethyltin chloride (3.11 g, 15.6 mmol), m.p. 37 °C, identified by its i.r. spectrum, collected on the cold finger, and 2,3-dichloro-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene (2) (4.55 g, 16.9 mmol, 84.5%) [Found: C, 31.2; F, 42.0%; *M* (mass spec.) 268 (for <sup>35</sup>Cl). C<sub>7</sub>Cl<sub>2</sub>F<sub>6</sub> requires C, 31.15; F, 42.4%; *M*, 268 (for <sup>35</sup>Cl)], b.p. 113–115 °C at 766 mmHg (Siwoloboff), n<sub>D</sub><sup>25</sup> 1.401, λ<sub>max</sub> (film) 5.68 (CF=CF str.) and 6.23 μm (CCl=CCl str.), δ<sub>F</sub> (neat liq.) +56.0 (CF<sub>2</sub>, AB system,

|J<sub>gem</sub>| 150 Hz, ν<sub>0δ</sub> 2.99 p.p.m.), +76.6 (CF:CF, narrow m), and +131.4 p.p.m. (≥CF, s) (rel. int. 2:2:2), condensed in the trap. Trimethyltin chloride (4.21 g, total 36.7 mmol, 92%) was recovered from the vessel.

**2,3-Dibromo-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene (3).**—Bromine (2.44 g, 15.25 mmol) was admitted to a cold (−196 °C) evacuated Pyrex tube (60 ml) containing 1,2,3,4,7,7-hexafluoro-5,6-bis(trimethylstannyl)bicyclo[2,2,1]hepta-2,5-diene (1) (3.99 g, 7.6 mmol) and carbon tetrachloride (7.67 g). The tube was sealed, *in vacuo*, with a 4 mm PTFE Fischer–Porter needle valve, stored for 36 h at −23 °C, then allowed to warm slowly to room temperature. The volatile product was separated by trap-to-trap fractional condensation at 1–2 mmHg into carbon tetrachloride (−196 °C trap) and a colourless liquid (6.40 g; −45 °C trap). A sample of the latter was separated by g.l.c. (4 m PEGA–Celite; 166 °C) into 2,3-dibromo-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene (3) (yield, by g.l.c. analysis of −45 °C fraction, 99%) [Found: C, 23.4; F, 31.8%; *M* (mass spec.) 356 (for <sup>79</sup>Br). C<sub>7</sub>Br<sub>2</sub>F<sub>6</sub> requires C, 23.5; F, 31.6%; *M*, 356 (for <sup>79</sup>Br)], b.p. 146.5–147.5 °C at 769 mmHg (Siwoloboff), n<sub>D</sub><sup>20</sup> 1.458, λ<sub>max</sub> (film) 5.69 (CF=CF str.) and 6.33 μm (CBr=CBr str.), δ<sub>F</sub> (neat liq.) +54.5 (CF<sub>2</sub>, AB system, |J<sub>gem</sub>| 145 Hz, ν<sub>0δ</sub> 1.85 p.p.m.), +74.8 (CF=CF, narrow m), and +125.9 p.p.m. (≥CF, s) (rel. int. 2:2:2), and trimethyltin bromide, identified by its i.r. spectrum.

**1,2,3,4,7,7-Hexafluoro-5,6-di-iodobicyclo[2,2,1]hepta-2,5-diene (5).**—A solution of iodine (3.90 g, 15.36 mmol) in carbon tetrachloride (4.0 g) was admitted to a cold (−196 °C) evacuated Pyrex tube (60 ml) containing 1,2,3,4,7,7-hexafluoro-5,6-bis(trimethylstannyl)bicyclo[2,2,1]hepta-2,5-diene (1) (4.09 g, 7.78 mmol) and carbon tetrachloride (3.52 g). The tube was sealed, *in vacuo*, with a 4 mm PTFE Fischer–Porter needle valve, then shaken for 2 days at room temperature. The volatile product was separated by trap-to-trap fractional condensation at 1–2 mmHg into carbon tetrachloride (−196 °C trap) and a colourless liquid (7.95 g, −45 °C trap). A sample of the latter was separated by g.l.c. (3 m SE30–Celite; 160 °C) into 1,2,3,4,7,7-hexafluoro-5,6-di-iodobicyclo[2,2,1]hepta-2,5-diene (5) (yield, by g.l.c. analysis of the −45 °C fraction, 99%) [Found: *M* (mass spec.) 452. C<sub>7</sub>I<sub>2</sub>F<sub>6</sub> requires *M*, 452], b.p. 168–169 °C at 750 mmHg (Siwoloboff), n<sub>D</sub><sup>20</sup> 1.519, λ<sub>max</sub> (film) 5.70 (CF=CF str.) and 6.51 μm (CI=CI str.), δ<sub>F</sub> (neat liq.) +53.9 (CF<sub>2</sub>, AB system, |J<sub>gem</sub>| 147 Hz, ν<sub>0δ</sub> 1.9 p.p.m.), +74.2 (CF=CF, s), and +115.5 p.p.m. (≥CF, s) (rel. into. 2:2:2), and trimethyltin iodide, identified by its i.r. spectrum.

**1,2,3,4,7,7-Hexafluorobicyclo[2,2,1]hepta-2,5-diene (4).**—Hydrogen chloride (0.14 g, 3.8 mmol) was condensed into a cold (−196 °C) evacuated Pyrex tube (60 ml) containing 1,2,3,4,7,7-hexafluoro-5,6-bis(trimethylstannyl)bicyclo[2,2,1]hepta-2,5-diene (1) (2.00 g, 3.82 mmol) and carbon tetrachloride (7.12 g); the tube was sealed, *in vacuo*, with a 4 mm PTFE Fischer–Porter needle valve, stored for 2 days at −23 °C, then allowed to warm slowly to room temperature. The volatile product was separated by trap-to-trap condensation at 1–2 mmHg into carbon tetrachloride (−196 °C trap) and a colourless liquid (2.08 g; −45 °C trap). A sample of the latter was separated by g.l.c. (3 m SE30–Celite; 80 °C) into 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene (4) (yield, by g.l.c. analysis of the −45 °C fraction, 90%) and trimethyltin chloride, both of which were identified by comparison of their i.r. spectra with those of authentic samples.

**Fluorination of 2,3-Dichlorohexafluorobicyclo[2,2,1]hepta-2,5-diene (2).**—With the cobalt trifluoride reactor heated to 70 °C, the two traps cooled to -72 and -196 °C, respectively, and the apparatus evacuated but isolated from the pump, the dichloride (1.12 g, 4.16 mmol) was allowed to vaporise and pass from the reservoir into the reactor. The product, trapped at -72 °C, showed no i.r. absorption below 6.8  $\mu\text{m}$ , gave only one peak when examined by g.l.c. (2 m Apiezon L-Celite; 74 °C), and gave the correct analytical figures for 2,3-dichlorodecafluorobicyclo[2,2,1]heptane (1.17 g, 3.39 mmol, 81.5%) (Found: C, 24.1.  $\text{C}_7\text{F}_{10}\text{Cl}_2$  requires C, 24.3%), m.p. 118–119 °C (sealed tube).

**Perfluorobicyclo[2,2,1]hept-2-ene (7).**—2,3-Dichlorodecafluorobicyclo[2,2,1]heptane (0.80 g, 2.32 mmol) in dry bis-(2-methoxyethyl) ether (10 ml) was added slowly (25 min) to a vigorously stirred suspension of activated <sup>6a</sup> zinc dust (20 g) in boiling dry bis-(2-methoxyethyl) ether (20 ml); the mixture was heated under reflux for 30 min while the vessel was purged with nitrogen, product being swept into a cold trap (-72 °C) *via* a water-cooled condenser. The product was separated by g.l.c. (3 m SE30-Celite; 70 °C) into perfluorobicyclo[2,2,1]hept-2-ene (7) (0.43 g, 1.57 mmol, 68%) [Found: C, 30.8; F, 69.2%; *M* (mass spec.) 274. Calc. for  $\text{C}_7\text{F}_{10}$ : C, 30.7; F, 69.3%; *M*, 274], m.p. 30–31 °C (sealed tube) (lit.,<sup>4</sup> 32–33 °C),  $\lambda_{\text{max}}$  (vapour) 5.67  $\mu\text{m}$  (CF=CF str.) (lit.,<sup>4</sup> 5.68  $\mu\text{m}$ ),  $\delta_{\text{F}}$  (30% w/w soln. in  $\text{CFCl}_3$ ; 94.1 MHz) +49.7 ( $\text{CF}_2\text{CF}_2$ , asymmetric m, presumably the centre lines of an AB-type system, the outer lines not being observable), +61.3 ( $\text{CF}_2$  bridge, AB-system,  $|J_{\text{gem}}|$  202 Hz,  $\nu_0\delta$  18.7 p.p.m.), +74.2 (CF:CF, s), and +147.7 p.p.m. ( $\text{CF}$ , narrow m) (the chemical shifts and assignments agree with literature<sup>4</sup> data, but the detailed band patterns do not), and 2-chloro-1,3,4,5,5,6,6,7,7-nonafluorobicyclo[2,2,1]hept-2-ene (0.17 g, 0.58 mmol, 25%),  $\lambda_{\text{max}}$  (vapour) 5.92  $\mu\text{m}$  (CF=CCl str.),  $\delta_{\text{F}}$  (neat liq.; 94.1 MHz) +49.8 ( $\text{CF}_2\text{CF}_2$ , asymmetric m), +51.7 (CF:CCl, m), +60.3 ( $\text{CF}_2$  bridge, AB-system,  $|J_{\text{gem}}|$  200 Hz,  $\nu_0\delta$  20.3 p.p.m.), +141.4 ( $\text{CF}$ ), and +145.3 p.p.m. ( $\text{CF}$ ), *m/e* 292 (highest mass,  $\text{C}_7\text{F}_9^{37}\text{Cl}^+$ , 11.3%), 221 (base peak,  $\text{C}_6\text{F}_8^{35}\text{Cl}^+$ ), and 290 ( $\text{C}_7\text{F}_9^{35}\text{Cl}^+$ , 36.4%).

**Photochemical Chlorination of 2,3-Dichlorohexafluorobicyclo[2,2,1]hepta-2,5-diene (2).**—A mixture of the diene (3.01 g, 11.2 mmol), chlorine (0.79 g, 11.1 mmol), and trichlorofluoromethane (*ca.* 2 g), sealed in a Pyrex ampoule (300 ml), was irradiated with light from a 300 W tungsten-filament lamp for 1 h. Volatile material was pumped out of the vessel, leaving an oil which was washed out with ether. Evaporation of the ether followed by vacuum sublimation of the residue yielded a white solid (3.10 g) which was separated by g.l.c. (2 m SE30-Celite; 160 °C; solution in ether injected) into 5,5,6,6-tetrachloro-1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (1.08 g, 3.18 mmol, 29%) (Found: C, 24.6; F, 33.1.  $\text{C}_7\text{F}_6\text{Cl}_4$  requires C, 24.7; F, 33.5%), m.p.

178–180 °C,  $\lambda_{\text{max}}$  (mull) 5.66  $\mu\text{m}$  (CF=CF str.),  $\delta_{\text{F}}$  (*ca.* 40% w/w soln. in  $\text{Et}_2\text{O}$ ) +49.8 ( $\text{CF}_2$ , AB system,  $|J_{\text{gem}}|$  182 Hz), +70.3 (CF:CF, s), and +129.5 p.p.m. ( $\text{CF}$ , s) (rel. int. 2 : 2 : 2), and 2,3,5,6-tetrachloro-1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hept-2-ene (2.04 g, 6.00 mmol, 54%) [Found: C, 24.4; F, 33.6%; *M* (mass spec.) 338 (for <sup>35</sup>Cl).  $\text{C}_7\text{F}_6\text{Cl}_4$  requires C, 24.7; F, 33.5%; *M*, 338 (for <sup>35</sup>Cl)], a low-melting volatile solid,  $\lambda_{\text{max}}$  (film) 6.20  $\mu\text{m}$  (CCl=CCl str.), the <sup>19</sup>F n.m.r. spectrum of which revealed the presence of at least two of the possible stereoisomers.

**Fluorination of a Mixture of 5,5,6,6-Tetrachloro-1,2,3,4,7,7- and 2,3,5,6-Tetrachloro-1,4,5,6,7,7-hexafluoro-bicyclo[2,2,1]hept-2-ene.**—The vapour of a mixture (2.13 g) of these isomers, prepared by photochemical chlorination of 2,3-dichlorohexafluorobicyclo[2,2,1]hepta-2,5-diene (2) as in the previous experiment, was pumped from the reservoir of the fluorination apparatus and over a bed of cobalt trifluoride heated to 75 °C; the traps were cooled to 0 and -196 °C. The product, which condensed in only the 0 °C trap, was a colourless, low-melting, solid (2.28 g) which showed no i.r. absorption below 7.4  $\mu\text{m}$  and gave five peaks on g.l.c. (2 m SE30-Celite; 150 °C); it was assumed to contain stereoisomeric tetrachloro-octafluorobicyclo[2,2,1]heptanes.

**Preparation of Perfluoronorbornadiene (6).**—A sample (2.16 g) of the presumed mixture of tetrachloro-octafluorobicyclo[2,2,1]heptanes from the previous experiment was dissolved in dry bis-(2-methoxyethyl) ether (5 ml) and added slowly (30 min) to a vigorously stirred suspension of activated <sup>6a</sup> zinc dust (20 g) in boiling bis-(2-methoxyethyl) ether (20 ml). The product, swept from the vessel with a stream of dry nitrogen into a cold (-72 °C) trap *via* a water-cooled condenser, was separated by g.l.c. (3 m SE30-Celite; 75 °C) into perfluorobicyclo[2,2,1]hepta-2,5-diene (6) (0.49 g) (Found: C, 35.3; F, 64.4.  $\text{C}_7\text{F}_8$  requires C, 35.6; F, 64.4%), b.p. 54.4 °C (isoteniscope),  $\lambda_{\text{max}}$  5.67 and 5.72  $\mu\text{m}$  (doublet, presumably owing to coupled oscillators) (CF=CF str.),  $\delta_{\text{F}}$  (neat liq.; 94.1 MHz) +57.4 ( $\text{CF}_2$ , symmetrical eleven-component narrow m), +77.8 (CF=CF, 5.3 Hz triplet), and +142.5 p.p.m. ( $\text{CF}$ , s), *m/e* 236 ( $M^{+}$ , 37.5%), 217 ( $\text{C}_7\text{F}_7^+$ , 41.3%), and 186 ( $\text{C}_6\text{F}_6^{+}$ , 100%), and 2-chloro-1,3,4,5,6,7,7-heptafluorobicyclo[2,2,1]hepta-2,5-diene (0.16 g) (Found: C, 33.3; F, 52.6.  $\text{C}_7\text{F}_7\text{Cl}$  requires C, 33.3; F, 52.7%), b.p. 87–88 °C at 764 mmHg (Siwoloboff),  $\lambda_{\text{max}}$  (vapour) 5.68 (CF=CF str.) and 5.93  $\mu\text{m}$  (CF=CCl str.),  $\delta_{\text{F}}$  (neat liq.; 94.1 MHz) +57.0 ( $\text{CF}_2$ , AB-system,  $|J_{\text{gem}}|$  147 Hz,  $\nu_0\delta$  0.6 p.p.m.), +57.4 (CF=CCl, s), +76.1 (CF=CF, s), +79.9 (CF=CF, s), +135.4 ( $\text{CF}$ , d), and +140.2 p.p.m. ( $\text{CF}$ , d), *m/e* 254 ( $\text{C}_7\text{F}_7^{37}\text{Cl}^+$ , 10.4%), 252 ( $\text{C}_7\text{F}_7^{35}\text{Cl}^+$ , 36.0%), 235 ( $\text{C}_7\text{F}_6^{37}\text{Cl}^+$ , 6.9%), 233 ( $\text{C}_7\text{F}_6^{35}\text{Cl}^+$ , 23.5%), 204 ( $\text{C}_6\text{F}_5^{37}\text{Cl}^+$ , 30.7%), and 202 ( $\text{C}_6\text{F}_5^{35}\text{Cl}^+$ , 100%).