



## Perfluorobarrelene

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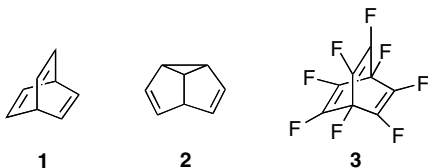
Photolysis

### ABSTRACT

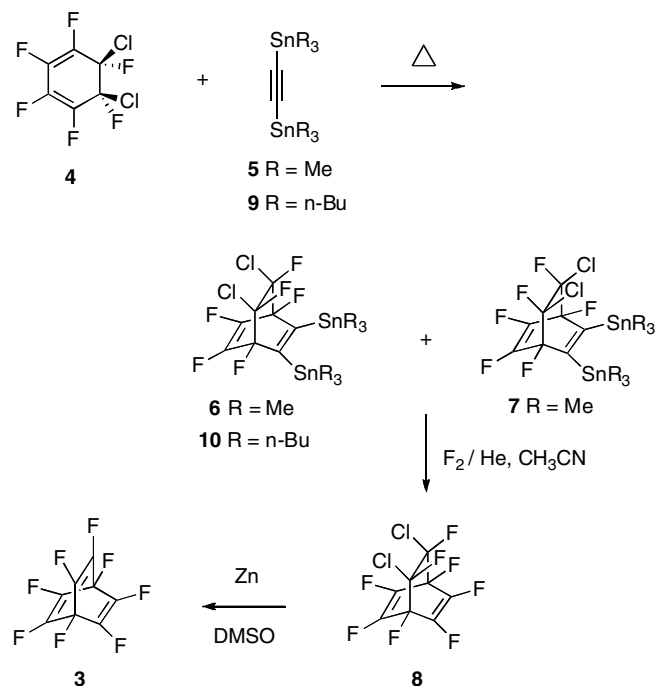
The title fluorocarbon has been synthesized in three steps from *cis*-5,6-dichlorohexafluorocyclohexa-1,3-diene, a hexafluorobenzene synthon. Photolysis of perfluorobarrelene yields perfluorocyclooctatetraene. An extremely facile *retro*-Diels–Alder reaction is also described.

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With its array of pi orbitals interacting through space in Möbius fashion, bicyclo[2.2.2]octa-2,5,7-triene (barrelene, **1**) is a particularly interesting hydrocarbon.<sup>1–4</sup> Sensitized photolysis of **1** yields semibullvalene (**2**), another unusual member of the manifold of (CH)<sub>8</sub> hydrocarbons that undergoes degenerate rearrangement with remarkable ease.<sup>5–8</sup> Because hydrocarbons and their fluorocarbon counterparts typically contrast in their properties and chemistry in ways that shed light on the effects of fluorine substitution,<sup>9</sup> we wished to synthesize perfluorobarrelene (**3**). We hoped, however, that the contrast would not extend to the photoisomerization reaction, as **3** might serve as a photoprecursor for the unknown perfluorosemibullvalene.



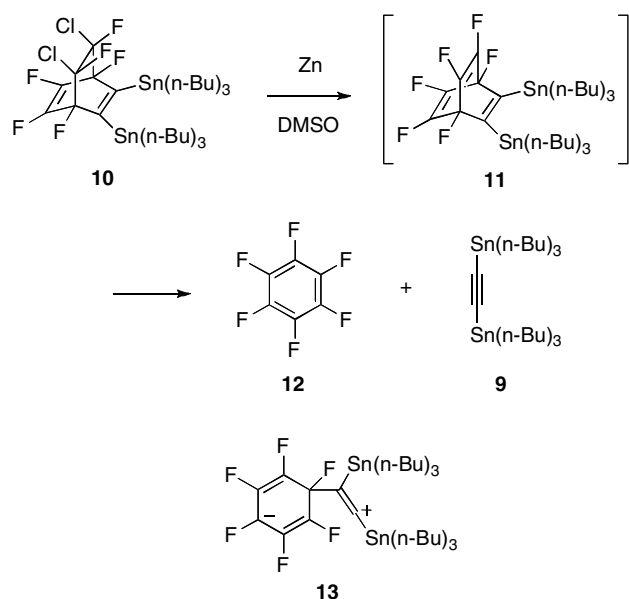
Synthesis of perfluorobarrelene,<sup>10</sup> outlined in Scheme 1, was greatly facilitated by the ready availability of 5,6-dichlorohexafluorocyclohexa-1,3-diene (**4**), a synthon for perfluorobenzene that had been prepared from that fluorocarbon in our laboratory in five steps and in >50% overall yield.<sup>11</sup> For addition to **4**, a synthon for the extremely labile difluoroacetylene<sup>12</sup> was needed. In principle,



Scheme 1.

chlorotrifluoroethylene could play that role, but it failed to react with diene **4** even at 180 °C for 24 h, presumably because of its electron-deficiency. Fortunately, the electron-rich bis(trimethylsilyl)acetylene (**5**) reacted smoothly with **4** at 85 °C to give a

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Scheme 2.

stereoisomeric mixture of Diels–Alder adducts **6** and **7** in the ratio 9:1 (87% yield). Fluorodestannylation of the mixture to afford chlorofluorocarbon **8** was accomplished with a stream of fluorine in helium (1:1) in acetonitrile at 0 °C (34% yield). To obtain perfluorobarrelene, **8** was dechlorinated with zinc in DMSO assisted by ultrasound<sup>13</sup> and with chromous chloride in dimethylformamide as well, albeit in quite low yield in each case.

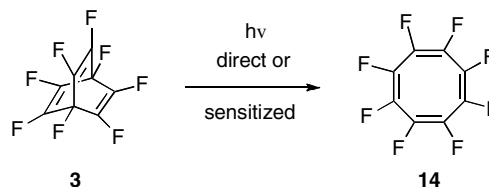
Because bis(trimethylstannyl)acetylene (**5**) is a highly toxic compound, the Diels–Alder reaction was also performed with its tributyl analog **9**.<sup>14</sup> The cycloaddition with **9** required more vigorous conditions (160 °C vs 85 °C), and gave a lower yield (51%<sup>15</sup>) of a single adduct (**10**);<sup>16</sup> the subsequent defluorostannylation reaction to afford **8** proceeded in 35% yield.<sup>15</sup> Bis(methylsilyl)acetylene reacted too in Diels–Alder fashion with diene **4** in 48 h at 150 °C (50% yield<sup>15</sup>), but fluorinolysis of the adduct<sup>17</sup> gave only polymeric products.

In an attempt to reverse the order of the fluorinolysis and dechlorination reactions, the tributylstannyl adduct **10** was subjected to zinc in DMSO with ultrasound, but surprisingly perfluorobenzene (**12**) was the only fluorine-containing product (Scheme 2). Monitoring the reaction by <sup>19</sup>F NMR revealed the intermediacy of triene **11** ( $\delta$  –157.5, 4 vinyl F; –194.5, 2 bridgehead Fs), which fragmented at rt. This extraordinarily facile *retro*-Diels–Alder reaction probably occurred via zwitterion **13** (or a transition state with the character of **13**), the negative charge being stabilized by conjugation and the positive charge by the  $\beta$ -C–Sn bond. Under the same conditions, the trimethylsilyl adduct behaved identically, presumably with assistance from the  $\beta$ -C–Si bond in the fragmentation step. C–Sn and C–Si bonds alpha to a positive charge also provide some stabilization by induction.

Perfluorobarrelene (**3**) is a highly volatile white solid, mp 68.5–70 °C (mp 15–16 °C for the parent hydrocarbon). Its <sup>19</sup>F NMR spectrum (CDCl<sub>3</sub>) comprises signals at  $\delta$  –150.1 and –219.0 ppm (3:1), representing the vinyl and bridgehead fluorines, respectively. The fluorocarbon displays double bond stretching absorption at 1746 cm<sup>–1</sup> in its infrared spectrum, corresponding to a band at 1580 cm<sup>–1</sup> for the parent. Its mass spectrum features a major molecular ion peak, the base peak corresponding to loss of CF<sub>3</sub>. Perfluorobarrelene has a maximum at 218 nm (log  $\epsilon$  = 2.9) (cyclohexane) in its ultraviolet spectrum, whereas the hydrocarbon gives

rise to two bands in the near UV at 208.0 nm (log  $\epsilon$  = 3.05) and 239 nm (log  $\epsilon$  = 2.48) (ethanol).<sup>1</sup>

Direct photolysis of **3** or sensitization with either acetone or benzene resulted in isomerization to perfluorocyclooctatetraene (**14**). None of the yet unknown perfluorosemibullvalene was obtained, despite the fact that under similar conditions semibullvalene (**2**) is the principal product from the parent barrelene (**1**).<sup>5c</sup>



## 1. Experimental

### 1.1. 7,8-Dichloro-2,3-bis(trimethylstannyl)perfluorobicyclo[2.2.2]octa-2,5-diene (**6**, **7**)

In a 25 mL round-bottomed flask were placed 10.39 g (29.6 mmol) of bis(trimethylstannyl) acetylene,<sup>18</sup> 7.65 g (29.8 mmol) of *cis*-5,6-dichlorohexafluorocyclohexa-1,3-diene,<sup>11</sup> and 2.5 g of calcium carbonate. *Caution*: Bis(trimethylstannyl)acetylene is a neurotoxin. The mixture was heated with stirring at 85 °C for 42 h (longer than necessary), then slurried in pentane, and placed on a column of silica gel (45 g). Elution with pentane gave the adduct as a white crystalline mass, 15.64 g (87% yield). Mp 70–71.5 °C. <sup>19</sup>F NMR (CDCl<sub>3</sub>) for **6** (90%):  $\delta$  –110.9 (2F, *gem* to Cl), –153.5 (2F, vinyl), –175.4 (2F, bridgehead); for **7** (10%):  $\delta$  –114.2 (2F, *gem* to Cl), –153.5 (2F, vinyl), –177.5 (2F, bridgehead). IR (KBr): 2980, 2910, 1760, 1340, 1285, 1220 cm<sup>–1</sup>. MS *m/e* (rel. int.): 593 (20%), 411 (56%), 361 (29%), 311 (22%), 257 (40%), 165 (100%). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>Cl<sub>2</sub>F<sub>6</sub>Sn<sub>2</sub>: C, 27.63; H, 2.98; Cl, 11.65; F, 18.73. Found: C, 27.39; H, 3.01; Cl, 11.82; F, 18.48.

### 1.2. 7,8-Dichloroperfluorobicyclo[2.2.2]octa-2,5-diene (**8**)

A solution of the adduct mixture **6** and **7** (17.7 g, 29.0 mmol) in 175 mL of acetonitrile contained in a cylindrical reactor (4.5 cm diam.) was cooled to 0 °C. A 1:1 mixture of fluorine in helium was bubbled into the bottom of the magnetically stirred solution at the rate of 15 mL/min for 16 h. *Caution*: Fluorine at high concentrations in helium is a very aggressive reagent. Reaction progress was monitored by <sup>19</sup>F NMR, and the gas inlet jet was occasionally unclogged with a copper wire. Sodium fluoride (8 g) was added late in the reaction to scavenge any HF that was formed, and could have been introduced at the outset. After trimethyltin fluoride had been removed by vacuum filtration, the reaction mixture was poured into cold water (250 mL). The yellow oil that separated was collected, then the aqueous phase was extracted with isopentane (3  $\times$  20 mL), and the extracts were combined with the yellow oil. This was followed by washing with water (100 mL) and 10% aqueous sodium bicarbonate (50 mL). The aqueous washings were back-washed with isopentane (2  $\times$  20 mL), and the combined organic extracts were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. Short-path distillation of the resulting yellow oil gave the diene as colorless, low-melting prisms, 3.13 g (34%). Bp 40–45 °C (11 Torr). <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  –116.0 (2F, *gem* to Cl), –150.4 (4F, vinyl), –209.1 (2F, bridgehead). IR (neat): 1780, 1755, 1350, 1280, 1245, 1150, 1053, 1000, 955, 795 cm<sup>–1</sup>.

### 1.3. Perfluorobicyclo[2.2.2]octatriene (3)

A 25 mL round-bottomed flask with a septum-capped sidearm and stir bar was clamped to a straight tube, which was clamped in turn to an oscillating motor. The tube was connected via vacuum tubing to a Firestone valve through which the system could be evacuated or filled with nitrogen. The flask was charged with freshly activated zinc dust (4.0 g, 0.06 mol) and dimethyl sulfoxide (DMSO, 7.0 mL, distilled from calcium hydride). After the system had been purged with nitrogen, dichloride **8** (0.918 g, 2.88 mmol) was introduced by syringe as a solution in DMSO, and the flask was rocked in an ultrasonic bath for 7 min at 21–23 °C. Following degassing by two freeze-pump-thaw cycles using liquid nitrogen, volatile product was vacuum transferred statically into the bottom of a small sublimator, while the reaction mixture was magnetically stirred. Sublimation at 11 Torr and 32 °C gave perfluorobarrelene as colorless prisms (0.125 g, 17.5%). Mp 58–60 °C. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>): δ –149.9 (6F, vinyl), –219.0 (2F, bridgehead). IR (vapor): 1746, 1332, 1260, 1145, 940, 895 cm<sup>-1</sup>. MS *m/e* (rel. int.): 248 (63%), 229 (30%), 210 (6%), 198 (46%), 186 (50%), 179 (100%). Through a combination of low temperature recrystallization from isopentane and sublimation, a sample melting at 68.5–70 °C was obtained.

#### Acknowledgment

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15. NMR yields; all others are isolated yields.
16. <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –110.6 (2F, gem to Cl), –154.3 (2F, vinyl), –174.8 (2F, bridgehead). <sup>1</sup>H NMR (CDCl<sub>3</sub>): bands in the δ 0.8–1.7 range.
17. <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ –111.4 (2F, gem to Cl), –153.5 (2F, vinyl), –183.7 (2F, bridgehead). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.34 (s, 18H).
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