

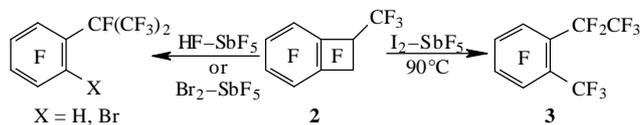
# Four-membered ring cleavage of perfluorinated benzocyclobutene and 1-methylbenzocyclobutene under the action of I<sub>2</sub>-SbF<sub>5</sub>

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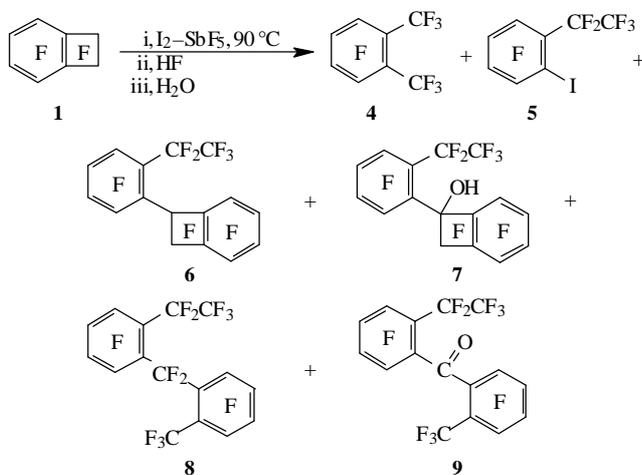
Interaction of perfluorobenzocyclobutene with I<sub>2</sub> in an SbF<sub>5</sub> medium leads to the formation of 2-iodoperfluoroethylbenzene and perfluoro-*o*-xylene; perfluoro-1-methylbenzocyclobutene in the I<sub>2</sub>-SbF<sub>5</sub> system is transformed into perfluoro-2-ethyltoluene.

Previously, we have found that benzocyclobutene **1** and perfluoro-1-methylbenzocyclobutene **2** under the action of Br<sub>2</sub> or HF in an SbF<sub>5</sub> medium undergo cleavage of the four-membered ring to give the corresponding 2-bromo- or 2-H-perfluoroalkylbenzenes.<sup>1–3</sup> Here we report a substantially different route to the ring opening of benzocyclobutenes **1** and **2** in the I<sub>2</sub>-SbF<sub>5</sub> system (about the I<sub>2</sub>-SbF<sub>5</sub> system<sup>4</sup>). We have found that compound **1** under the action of I<sub>2</sub> in an SbF<sub>5</sub> medium gives not only the cleavage product of the C<sup>Ar</sup>-C<sup>1</sup> bond of the four-membered ring (as in the case of Br<sub>2</sub> or HF<sup>1,2</sup>), but the product of C<sup>1</sup>-C<sup>2</sup> bond cleavage as well. At the same time, compound **2** undergoes only of the C<sup>1</sup>-C<sup>2</sup> bond cleavage.

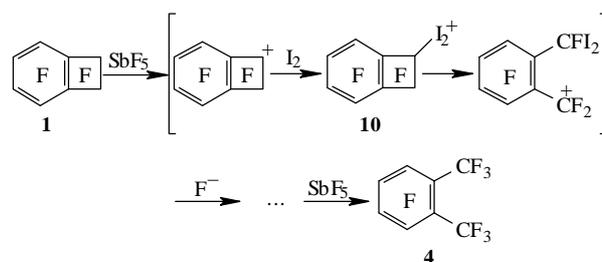


Thus, when heated with I<sub>2</sub> in an SbF<sub>5</sub> medium, compound **2** is transformed to perfluoro-2-ethyltoluene **3**<sup>†</sup> (Scheme 1). Under the same conditions compound **1** gives perfluoro-*o*-xylene **4** together with 2-iodoperfluoroethylbenzene **5**. In addition to these products, the reaction mixture contained perfluoro-2-(1-benzocyclobutenyl)ethylbenzene **6**, perfluoro-2-(1-hydroxy-1-benzocyclobutenyl)ethylbenzene **7**, perfluoro-2-ethyl-2'-methyl-diphenylmethane **8** and perfluoro-2-ethyl-2'-methyl-benzophenone **9**<sup>‡</sup> (Scheme 2).

Compound **6** is formed as a result of dimerisation of benzocyclobutene **1** in an SbF<sub>5</sub> medium.<sup>1</sup> Compound **8** seems to be the product of further transformations of dimer **6** under the reaction conditions (these transformations did not proceed under the action of SbF<sub>5</sub> at 90 °C in the absence of I<sub>2</sub>). It may be suggested that oxygen-containing compounds **7** and **9** are the hydrolysis products of cation salts, which seems to be formed from precursors **6** and **8** in an SbF<sub>5</sub> medium (*cf.* refs.5,6).



<sup>†</sup> Compound **3** was described by us earlier.<sup>1</sup>



Formation of compound **5** from benzocyclobutene **1** under the action of I<sub>2</sub> in an SbF<sub>5</sub> medium may be represented by a scheme similar to that for reactions of polyfluorobenzocyclobutenes with Br<sub>2</sub> or HF in an SbF<sub>5</sub> medium.<sup>1–3</sup> One of the possible routes of transformation of compound **1** to xylene **4** in the I<sub>2</sub>-SbF<sub>5</sub> system includes intermediate formation of cation **10** (Scheme 3). The latter may be considered as a heteroatomic analogue of perfluorobenzocyclobutenylalkyl cations for which a similar mechanism of four-membered ring cleavage was discussed.<sup>7</sup>

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<sup>‡</sup> Typical experimental procedure. Benzocyclobutene **1** (5.07 g, 20.4 mmol) was added to a stirred solution of 5.18 g (20.4 mmol) I<sub>2</sub> in 31.0 g (143 mmol) of SbF<sub>5</sub>. The mixture was stirred for 5 h 45 min at 90 °C, then cooled to -10 °C, treated with 6 ml of anhydrous HF and poured on to ice cooled with liquid N<sub>2</sub>. The mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined extracts dried over MgSO<sub>4</sub>. The solvent was distilled off to give 4.08 g of a mixture containing (GLC, <sup>19</sup>F NMR spectrum) 20% of ethylbenzene **5**, 28% of xylene **4**, 6% of dimer **6**, 4% of product **7**, 17% of diphenylmethane **8** and 22% of benzophenone **9**. Individual compounds **4–9** were isolated by preparative GLC. The <sup>19</sup>F NMR spectra of compounds **4** and **6** are in agreement with those reported in literature.<sup>8,1</sup> New compounds **5**, **7–9** exhibited satisfactory analytical data.

<sup>19</sup>F NMR spectra, ( $\delta$ /ppm downfield from C<sub>6</sub>F<sub>6</sub> as internal standard).

**5** (in CCl<sub>4</sub>, 56.4 MHz): 78.2 (CF<sub>3</sub>), 58.3 (F-3), 55.5 (CF<sub>2</sub>), 32.2 (F-6), 16.7 (F-4), 11.2 (F-5), *J*<sub>F-6, CF<sub>3</sub></sub> 40 Hz (*cf.* ref. 1).

**7** (in CDCl<sub>3</sub>, 188.3 MHz): 81.4 (CF<sub>3</sub>), 62.5 (F<sub>A</sub>) and 51.2 (F<sub>B</sub>, CF<sub>2</sub>CF<sub>3</sub>), *J*<sub>AB</sub> 285 Hz, 68.5 (F<sub>A</sub>) and 56.8 (F<sub>B</sub>, CF<sub>2</sub>), *J*<sub>AB</sub> 220 Hz, 33.4 (1F), 27.7 (1F), 26.1 (1F), 24.6 (1F), 18.9 (1F), 16.1 (2F), 13.2 (1F).

**8** (in CHCl<sub>3</sub>, 188.3 MHz): 108.7 (CF<sub>3</sub>), 92.3 (CF<sub>2</sub>), 80.7 (CF<sub>2</sub>CF<sub>3</sub>), 62.5 (F<sub>A</sub>) and 59.4 (F<sub>B</sub>, CF<sub>2</sub>CF<sub>3</sub>), *J*<sub>AB</sub> 280 Hz, 35.0 (1F), 30.6 (1F), 30.1 (1F), 29.3 (1F), 17.0 (1F), 15.8 (2F), 15.3 (1F).

**9** (in Me<sub>2</sub>CO, 56.4 MHz): 109.6 (CF<sub>3</sub>), 80.9 (CF<sub>2</sub>CF<sub>3</sub>), 59.7 (CF<sub>2</sub>CF<sub>3</sub>), 17.9–15.2 (4F), 32.0 (1F), 29.1 (1F), 27.1 (1F), 25.9 (1F).

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