Four-membered ring cleavage of perfluorinated benzocyclobutene and 1-methylbenzocyclobutene under the action of I_2–SbF_5

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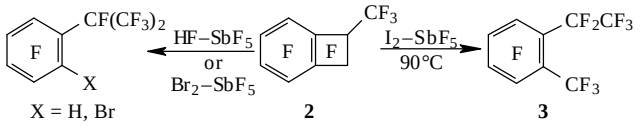
Interaction of perfluorobenzocyclobutene with I_2 in an SbF_5 medium leads to the formation of 2-iodoperfluoroethylbenzene and perfluoro-*o*-xylene; perfluoro-1-methylbenzocyclobutene in the I_2–SbF_5 system is transformed into perfluoro-2-ethyltoluene.

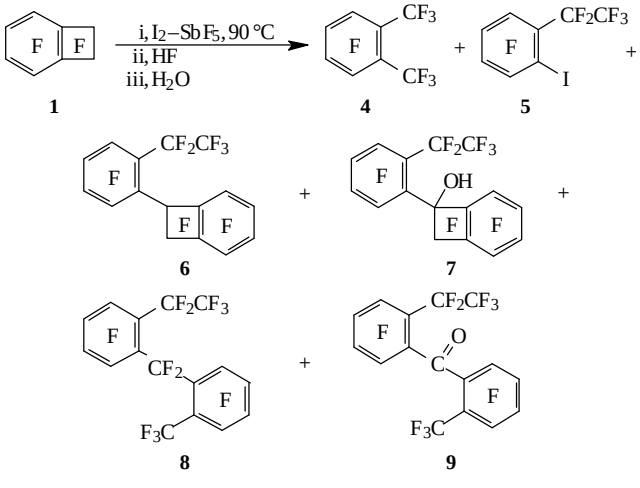
Previously, we have found that benzocyclobutene **1** and perfluoro-1-methylbenzocyclobutene **2** under the action of Br_2 or HF in an SbF_5 medium undergo cleavage of the four-membered ring to give the corresponding 2-bromo- or 2-H-perfluoroalkylbenzenes.[1–3] Here we report a substantially different route to the ring opening of benzocyclobutenes **1** and **2** in the I_2–SbF_5 system (about the I_2–SbF_5 system[4]). We have found that compound **1** under the action of I_2 in an SbF_5 medium gives not only the cleavage product of the C^{Ar}–C^1 bond of the four-membered ring (as in the case of Br_2 or HF[1,2]), but the product of C^1–C^2 bond cleavage as well. At the same time, compound **2** undergoes only of the C^1–C^2 bond cleavage.



Scheme 1

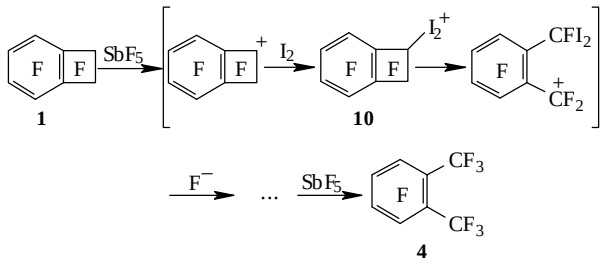
Thus, when heated with I_2 in an SbF_5 medium, compound **2** is transformed to perfluoro-2-ethyltoluene **3**† (Scheme 1). Under the same conditions compound **1** gives perfluoro-*o*-xylene **4** together with 2-iodoperfluoroethylbenzene **5**. In addition to these products, the reaction mixture contained perfluoro-2-(1-benzocyclobutenyl)ethylbenzene **6**, perfluoro-2-(1-hydroxy-1-benzocyclobutenyl)ethylbenzene **7**, perfluoro-2-ethyl-2'-methyldiphenylmethane **8** and perfluoro-2-ethyl-2'-methylbenzophenone **9**‡ (Scheme 2).

Compound **6** is formed as a result of dimerisation of benzocyclobutene **1** in an SbF_5 medium.[1] 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_5 at 90 °C in the absence of I_2). 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_5 medium (*cf*. refs.5,6).



Scheme 2

† Compound **3** was described by us earlier.[1]



Scheme 3

Formation of compound **5** from benzocyclobutene **1** under the action of I_2 in an SbF_5 medium may be represented by a scheme similar to that for reactions of polyfluorobenzocyclobutenes with Br_2 or HF in an SbF_5 medium.[1–3] One of the possible routes of transformation of compound **1** to xylene **4** in the I_2–SbF_5 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.[7]

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‡ *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_2 in 31.0 g (143 mmol) of SbF_5. 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_2. The mixture was then extracted with CH_2Cl_2 and the combined extracts dried over $MgSO_4$. The solvent was distilled off to give 4.08 g of a mixture containing (GLC, ^{19}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 ^{19}F NMR spectra of compounds **4** and **6** are in agreement with those reported in literature.[8,1] New compounds **5**, **7**–**9** exibited sutisfactory analytical data.

^{19}F NMR spectra, (δ/ppm downfield from C_6F_6 as internal standard).

5 (in CCl_4, 56.4 MHz): 78.2 (CF_3), 58.3 (F-3), 55.5 (CF_2), 32.2 (F-6), 16.7 (F-4), 11.2 (F-5), $J_{F\text{-}6,\,CF_3}$ 40 Hz (*cf*. ref. 1).

7 (in $CDCl_3$, 188.3 MHz): 81.4 (CF_3), 62.5 (F_A) and 51.2 (F_B, CF_2CF_3), J_{AB} 285 Hz, 68.5 (F_A) and 56.8 (F_B, CF_2), J_{AB} 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 $CHCl_3$, 188.3 MHz): 108.7 (CF_3), 92.3 (CF_2), 80.7 (CF_2CF_3), 62.5 (F_A) and 59.4 (F_B, CF_2CF_3), J_{AB} 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_2CO, 56.4 MHz): 109.6 (CF_3), 80.9 (CF_2CF_3), 59.7 (CF_2CF_3), 17.9–15.2 (4F), 32.0 (1F), 29.1 (1F), 27.1 (1F), 25.9 (1F).

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