Octafluorobicyclo[2.2.0]hex-1(4)-ene: A Greatly Strained Alkene with Novel Reactivity

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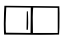
The hydrocarbon bicyclo[2.2.0]hex-1(4)-ene (**1**), which was prepared and studied by the Wiberg group,[1] is highly reactive as a consequence of its severe angle strain.[2] With the expectation that its fully fluorinated analog **2** would manifest very different but comparably interesting chemistry, we have synthesized this perfluoroalkene and trapped it with a variety of reagents.[3,4]



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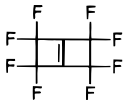

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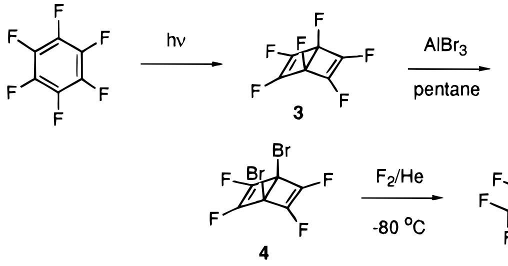
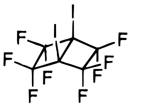
A precursor for **2**, dibromide **5**, was prepared in three steps from hexafluorobenzene as shown in Scheme 1. Vapor-phase photoisomerization[7,8] of the benzene to its Dewar isomer **3** was followed by treatment with aluminum bromide to effect selective replacement of the bridgehead fluorines with bromines, giving **4**.[9] Because it aromatizes even in the cold and especially because it tends to detonate capriciously, **4** was generally carried on without purification. Low temperature fluorination with 30% fluorine/helium transformed **4** into saturated dibromide **5**.[10]

Treatment of **5** with alkyllithiums at low temperatures or with zinc assisted by ultrasound yielded the desired alkene **2**, as revealed by trapping experiments. The electron-deficient alkene was susceptible to attack by the reagents required for its generation, however, so a precursor was sought that would release it under gentler conditions. Diiodide **6**, with its much weaker carbon−halogen bonds, was an appealing choice, but it could not be synthesized analogously to dibromide **5**. Efforts to make the very labile Dewar benzene **7** were successful,[11] but not surprisingly low-temperature fluorination of **7** gave a hopeless mixture.

Scheme 1





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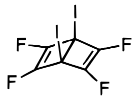

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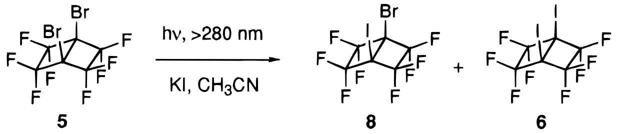
We discovered that the bromines in **5** can be replaced with iodines via an electron-transfer process. Ultraviolet irradiation of an acetonitrile solution of **5** and potassium iodide yields a mixture of bromoiodide **8**[12] and diiodide **6**.[13] Either can be made the dominant product, and **6** can be obtained in high yield when the reaction is carried out in a mixture of acetonitrile and ether. We suggest the name "photo-Finkelstein reaction" for this transformation; although its mechanism is very different from that of its namesake, like the Finkelstein reaction[14] it accomplishes the replacement of other halogens by iodine through the agency of iodide ion.



Treatment of either **6** or **8** with mercury or silver in the presence of ultrasound generated alkene **2** very cleanly (Scheme 2). The Diels−Alder adduct **9** was the sole product when the reaction was carried out in the presence of furan.[15] Nucleophilic

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[1] (a) Wiberg, K. B.; Maturro, M. G.; Okarma, P. J.; Jason, M. E.; Dailey, W. P.; Burgmaier, G. J.; Bailey, W. F.; Warner, P. *Tetrahedron* **1986**, *42*, 1895. (b) Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 2194. Wiberg, K. B.; Bailey, W. F.; Jason, M. E. *J. Org. Chem.* **1974**, *39*, 3803. Casanova, J.; Rogers, H. R. *J. Org. Chem.* **1974**, *39*, 3803. Wiberg, K. B.; Burgmaier, G. J.; Warner, P. *J. Am. Chem. Soc.* **1971**, *93*, 246.

[2] Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710.

[3] This paper is based principally on the Ph.D. dissertation of Y.Z., Dartmouth College, 1995.

[4] Analysis of the infrared spectrum of the parent hydrocarbon **1** has shown it to be planar (ref 1a), confirming the conclusion from ab initio quantum mechanical calculations (refs 2 and 5). By demanding more p character from the central carbons, perfluoroalkyl substituents on the double bond might force pyramidalization of that bond, as is predicted for such strained alkenes as an isomer of **1**, bicyclo[3.1.0]hex-1(5)-ene (refs 5 and 6). We find, however, that calculations up to the 6-31G** level predict fluorocarbon **2** to be planar like **1**. These calculations were carried out with the Spartan package of programs (Hehre, W.; Wavefunction, Inc.: 18401 Von Karman, Suite 370, Irvine, CA 92717).

[5] Wagner, H.-U.; Szeimes, G.; Chandrasekhar, J; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210.

[6] Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85.

[7] Barlow, M. G.; Haszeldine, R. N.; Morton, W. D.; Woodward, D. R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2170.

[8] Camaggi, G.; Gozzo, F. *J. Chem. Soc.* **1969**, 489.

[9] Camaggi and Gozzo prepared the dichloro analog of **4** from **3** and aluminum chloride (ref 8).

[10] ^{19}F NMR ($CDCl_3$): Φ −103.9 (4 exo F), −113.4 (4 endo F) (AB q, $J = 219$ Hz). HRMS *m/e*: 383.8222 (calcd 383.8219). Mp: 81.5−83 °C.

[11] The reaction of **3** with aluminum iodide had been carried out earlier by Camaggi and Gozzo (ref 8), but instead of **7** they obtained its aromatic isomer.

[12] ^{19}F NMR of **8** ($CDCl_3$): Φ −92.3 (exo F_3, F_5), −112.5 (endo F_3, F_5) (AB q, $J = 220.1$ Hz), −102.2 (exo F_2, F_6), −113.1 (endo F_2, F_6) (AB q, $J = 220.7$ Hz). HRMS *m/e*: 429.8080 (calcd 429.8100). Mp: 79−80 °C.

[13] ^{19}F NMR of **6** ($CDCl_3$): Φ −90.8 (4 exo F), −112.1 (4 endo F) (AB q, $J = 216$ Hz). HRMS *m/e*: 477.7943 (calcd 477.7962). Mp: 112.5−113.5 °C.

[14] Finkelstein, H. *Chem. Ber.* **1910**, *43*, 1528.

[15] ^{19}F NMR of **9** ($CDCl_3$): Φ −113.2 (2 endo F), −114.8 (2 exo F) (AB q, $J = 224.1$ Hz), −115.3 (2 endo F), −121.7 (2 exo F) (AB q, $J = 228.4$ Hz). The endo fluorine signals are each subsplit into doublets ($J = 48$ Hz) as a consequence of through-space interaction; apparently nonbonded repulsions between bridges in this ring system splay them apart, thus pressing together the endo fluorines. For the same reason, the vinyl hydrogens are coupled to the neighboring exo fluorines. ^{1}H NMR ($CDCl_3$): δ 6.35 (d, $J_{HF} = 7.5$ Hz, 2 vinyl H), 5.35 (s, 2 bridgehead H). HRMS *m/e*: 292.0124 (calcd 292.0134). Mp: 124.5−126 °C.

[16] ^{19}F NMR of **10** ($CDCl_3$): Φ −112.0, −115.6 (AB q, $J = 226$ Hz, 4 F), −113.8, −124.6 (AB q, $J = 222$ Hz, 4 F). ^{1}H NMR ($CDCl_3$): δ 3.95 (s, 3 H), 2.01 (s, 1 H). HRMS: 256.0132 (calcd 256.0134).

[17] ^{19}F NMR of **12** ($CDCl_3$): Φ −105.7 (s, 2 F), −120.4 (s, 2 F), −121.8 (m, 1 F), −133.3 (s, 2 F). ^{1}H NMR: δ 5.9 (1 H), 4.0 (2 H). MS (CI) *m/e*: 258 (MNH_4^+), 220 ($M^+ - HF$), 175 (base, $C_4F_5O_2^+$). IR: 1627 ($\nu_{C=C}$), 3500 cm^{-1} (br, ν_{OH}).

[18] Hydration of highly fluorinated ketones is very exothermic. Guthrie, J. P. *Can. J. Chem.* **1975**, *53*, 898. Hine, J.; Flackstean, H. *J. Org. Chem.* **1979**, *42*, 177.

[19] ^{19}F NMR of **13** ($CDCl_3$): Φ −106.0, −113.2 (AB q, $J = 223$ Hz, 2 F), −107.9, −118.4 (AB q, $J = 218$ Hz, 2 F), −109.0, −119.0 (AB q, $J = 213$ Hz, 2 F), −110.7, −111.5 (AB q, $J = 216$ Hz, 2 F). ^{1}H NMR: δ 4.61 (br t, $J = 7.9$ Hz, CH), 3.52, 3.41 (q of AB q, $J = 7.1$ Hz, $J_{AB} = 9.3$ Hz, OCH_2), 3.09 (m, ring CH_2), 1.22 (t, $J = 7.1$, CH_3).

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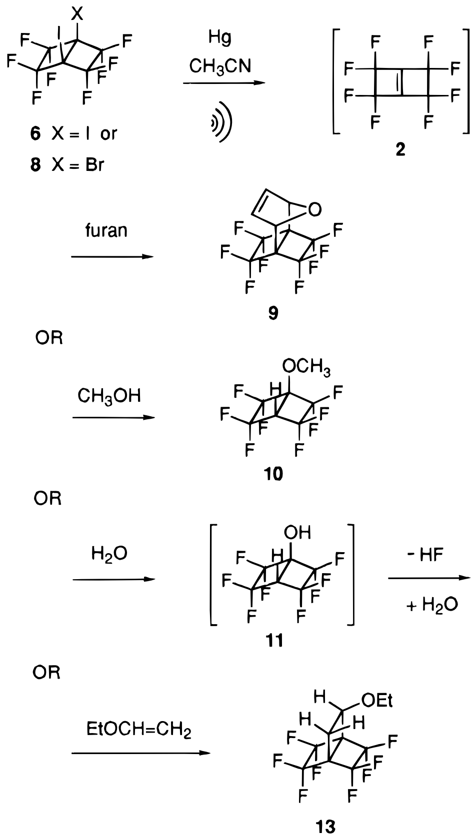
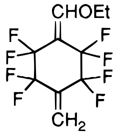
Scheme 2



attack on **2** by methanol gave **10** in high yield.[16] When water was present in the reaction mixture, *gem*-diol **12** was obtained.[17] Initial adduct **11** ring opened under the reaction conditions with loss of hydrogen fluoride, and the resulting cyclohexenone hydrated to give **12**.[18] Remarkably, ethyl vinyl ether trapped alkene **2** as the [2.2.2]propellane **13**.[19] This represents a novel route to the highly strained [2.2.2]propellanes, only one of which (a carboxamido derivative[20]) has ever been isolated.[21,22] Upon standing at room temperature, **13** slowly ring opens smoothly to **14**[23] and **15**[24] (70:30), thus providing confirmation of its structure.[25]



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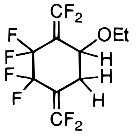

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When no trapping agent is present in the mercury-induced dehalogenation of **6** or **8**, a mercury complex of alkene **2** is formed; we have not yet succeeded in observing the free alkene. Ultraviolet irradiation of diiodide **6** may make that possible, since trapping experiments have shown that this photolysis does generate **2**. Future efforts will be directed toward characterization of the alkene, further investigation of its reactivity, and study of derived propellanes.

Acknowledgment. The authors thank the National Science Foundation for support of this research. High-resolution and chemical ionization mass spectra were run by Dr. Andrew Tyler at the Harvard University Mass Spectrometry Laboratory, supported by NSF Grant CHE 9020043 and NIH Grant 510-RR06716, and by the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln.

JA961656O

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(20) Eaton, P. E.; Temme, G. E., III *J. Am. Chem. Soc.* **1973**, *95*, 7508.

(21) The parent [2.2.2]propellane may have been generated and trapped, although it has not been directly observed. Wiberg has shown that studies suggesting the formation of the propellane by treatment of bridgehead dihalides with reducing agents can be interpreted without intervention of the propellane (Wiberg, K. B.; Pratt, W. E.; Matturro, M. G. *J. Org. Chem.* **1982**, *47*, 2720). Generation of [2.2.2]propellane by photocyclization of 1,4-dimethylenecyclohexane has been claimed by Dannenberg et al. Dannenberg, J. J.; Prociv, T. M.; Hutt, C. *J. Am. Chem. Soc.* **1974**, *96*, 913.

(22) Parent alkene **1** dimerizes, yielding a diene which must have formed via a transient bis[2.2.2]propellane. Alkene **1** also adds to ketene to give a product which is presumably derived from an intermediate [2.2.2]propellane (ref 1).

(23) ^{19}F NMR of **14** (CDCl$_3$): Φ −112.8 (s, 2 F), −114.5 (s, 2 F), −118.7 (s, 2 F), −119.2 (s, 2 F). ^{1}H NMR: δ 7.13 (s, CH), 6.31 (s, C=CH$_2$), 4.16 (q, J = 7.2 Hz, OCH$_2$), 1.37 (t, J = 7.2 Hz, CH$_3$). MS (*m*/*e*): 296 (M$^+$), 219 ($C_7H_5F_6O^+$), 127 ($C_4H_3F_4^+$). HRMS: 296.0450 (calcd 296.0447).

(24) ^{19}F NMR of **15** (CDCl$_3$): Φ −73.8, −75.3, −78.0, −80.1 (4 vinyl F), −102.3, −126.4 (AB q, J = 260 Hz, CF$_2$), −108.1, −131.2 (AB q, J = 260 Hz, CF$_2$). ^{1}H NMR: δ 4.38 (br s, CH), 3.47, 3.35 (subsplit AB q, OCH$_2$), 2.81, 2.35 (subsplit AB q, J_{AB} = 15.3 Hz, ring CH$_2$), 1.16 (t, J = 6.9 Hz, CH$_3$). MS (*m*/*e*): 296 (M$^+$), 268 ($M^+ - C_2H_4$), 251 ($M^+ - C_2H_5O$), 231 ($C_8H_2F_7^+$), 219 ($C_7H_5F_6O^+$), 200 ($C_7H_5F_5O^+$), 181 ($C_7H_5F_4O^+$), 127 ($C_4H_3F_4^+$). HRMS: 296.0453 (calcd 296.0447).

(25) For the mechanism of ring opening of [2.2.2]propellanes, see: Wiberg, K. B.; Caringi, J. J.; Matturro, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 5854. Newton, M. D.; Schulman, J. M. *Ibid.* **1972**, *94*, 4391. Stohrer, W.-D.; Hoffmann, R. *Ibid.* **1972**, *94*, 779.