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# Triscycloproparenes

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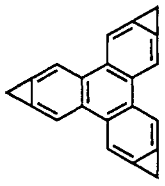
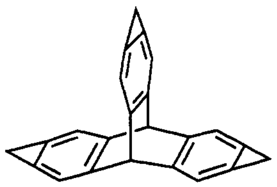
Cycloproparenes are the most highly strained members of the 1,2-bridged aromatic hydrocarbons.[1] The first cycloproparene was isolated by Anet and Anet[2] in 1964, and a synthesis of the parent hydrocarbon was reported in 1965 by Vogel, Grimme, and Korte.[3] Subsequent work led to the development of additional routes to the cycloproparenes, and for the most part, the simple members of this family are now readily available. Although the synthesis of biscycloproparenes has been described,[4,5] triscycloproparenes are unknown. We report here the syntheses of the triscycloproparenes **1** and **2**, compounds that are of interest to us as precursors to graphitic-like networks with holes or to honeycomb structures.[6]



**1**

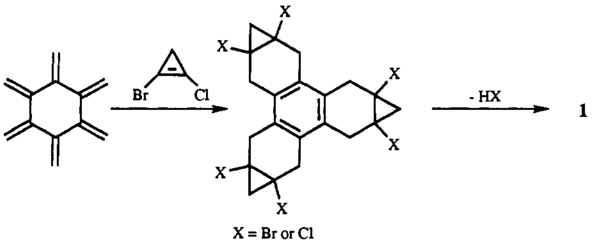


**2**

1-Bromo-2-chlorocyclopropene,[7] a versatile cycloproparene synthon, was used in a key step during the synthesis of each cycloproparene. The synthesis of **1** is presented in Scheme 1.[8] Conversion of the complicated mixture of isomers of **3** to the cycloproparene **1** was carried out (20% isolated yield) under an atmosphere of nitrogen by addition of the starting material to potassium *tert*-butoxide in tetrahydrofuran at −50 °C and subsequent warming to room temperature. Purification of the white solid **1** was achieved by flash column chromatography on neutralized Florisil (hexane).

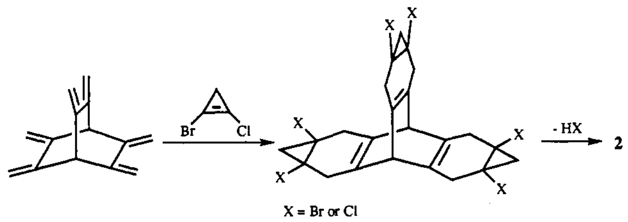
The $^1$H NMR spectrum of **1**[9] (250 MHz, $CDCl_3$) exhibits two sharp singlets at $\delta$ 3.59 and 8.66. The $^{13}$C NMR spectrum has signals at 19.5, 109.9, 125.3, and 133.2 ppm. The high-field shift at 109.9 is typical of carbons ortho to the cyclopropyl ring.[1] This signal is found at 114.7 ppm for benzocyclopropene. An infrared band (weak) characteristic of cycloproparenes is observed at 1670 cm$^{-1}$. Other bands were observed at 2956, 2919, 1736, 1721, 1590, 1477, 1435, 1364, 1294, 1256, 1157, 1054, and 833 cm$^{-1}$. The ultraviolet spectrum recorded in *n*-hexane has $\lambda_{max}$ at 272 nm ($\epsilon$ 6.5 × $10^4$). Weaker absorptions were found at 254, 264, 288, 300, and 322 nm.

**Scheme 1**



**3**

**Scheme 2**

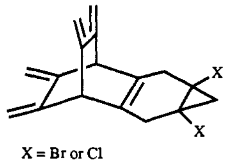


**4**

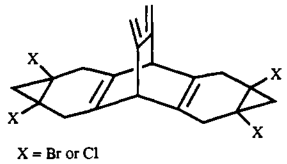
The synthesis of **2** is presented in Scheme 2. The starting material **4** could be prepared by repetitive addition of 1-bromo-2-chlorocyclopropene to hericene.[10] The elimination of **4** could not be effected using potassium *tert*-butoxide in tetrahydrofuran as described for the synthesis of **1**; however, a mixture of *N,N*-dimethylformamide, hexamethylphosphoramide (5:1), and potassium *tert*-butoxide at room temperature under an atmosphere of nitrogen provided a suitable medium to carry out this reaction. The cycloproparene could be isolated as a white solid in about 50% yield.

The $^1$H NMR spectrum (300 MHz, acetone-$d_6$) of **2** exhibits signals at $\delta$ 3.16 (6H), 5.81 (2H), and 7.37 (6H). $^{13}$C NMR signals were observed at 21.8, 55.3, 112.0, 124.0, and 147.8 ppm. HRMS: calcd for $C_{23}H_{14}$ *m/e* 290.1096, found 290.1094. The fascinating compounds prepared by Hart and his co-workers[11] provide excellent models for structural identification of this cycloproparene.

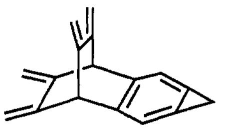
The Diels–Alder adducts **5** and **6** were also isolated from the reaction of hericene with 1-bromo-2-chlorocyclopropene. These compounds could be purified by preparative TLC on silica (isooctane) and converted to the cycloproparenes **7** and **8**, respectively, using potassium *tert*-butoxide dissolved in the *N,N*-dimethylformamide–hexamethylphosphoramide medium used to synthesize **2**.



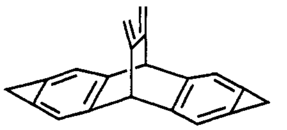
**5**



**6**



**7**



**8**

The $^1$H NMR spectrum (250 MHz, acetone-$d_6$) of the white solid **7** (65% yield) exhibits signals at $\delta$ 3.20 (q, 2H), 4.56 (s, 2H),

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[1] Reviews: Billups, W. E.; Rodin, W. A.; Haley, M. M. *Tetrahedron* **1988**, *44*, 1305. Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349; *Chem. Rev.* **1989**, *89*, 1161.

[2] Anet, R.; Anet, F. A. L. *J. Am. Chem. Soc.* **1964**, *86*, 525.

[3] Vogel, E.; Grimme, W.; Korte, S. *Tetrahedron Lett.* **1965**, 3625.

[4] Ippen, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 736. Halton, B.; Boese, R.; Bläser, D.; Lu, Q. *Aust. J. Chem.* **1991**, *44*, 265.

[5] Billups, W. E.; Haley, M. M.; Claussen, R. C.; Rodin, W. A. *J. Am. Chem. Soc.* **1991**, *113*, 4331.

[6] This expectation is based on our earlier work, which has shown that cycloproparenes can be dimerized by silver ion in chloroform to yield linear dimers connected by six-membered rings. See: Billups, W. E.; McCord, D. J.; Maughon, B. R. *Tetrahedron Lett.* **1994**, *35*, 4493.

[7] Billups W. E.; Lin. L.-J.; Arney, B. E., Jr.; Rodin, W. A.; Casserly E. W. *Tetrahedron Lett.* **1984**, 3935.

[8] The hexaradialene was synthesized as described by Schiess and Heitzmann. See: Schiess, P.; Heitzmann, M. *Helv. Chim. Acta* **1978**, *61*, 844.

[9] Due to extensive fragmentation under an expansive set of conditions it was not possible to obtain the HRMS of the parent molecular ion of **1**.

[10] Hericene was prepared as described by Köhler and Steck. See: Köhler, F. H.; Steck, A. *J. Organomet. Chem.* **1993**, *444*, 165. For the first reported synthesis of hericene, see: Pilet, O.; Birnbaum J.-L.; Vogel, P. *Helv. Chim. Acta* **1983**, *66*, 19. For the origin of the name, see: Nickon, A.; Silversmith, E. *The Name Game*; Pergamon Press: New York, 1987.

[11] Bashir-Hashami, A.; Hart, H.; Ward, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 6675.

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5.10 (s, 4H), 5.33 (s, 4H), and 7.22 (s, 2H). $^{13}C$ ($CDCl_3$) NMR signals were observed at 20.2, 57.6, 105.1, 111.0, 125.2, 144.1, and 144.2 ppm. HRMS: calcd for $C_{17}H_{14}$ *m/e* 218.1096, found 218.1095. Compound **8** was isolated as a white solid in 69% yield (mp 110 °C dec). $^1H$ signals (250 MHz, acetone-$d_6$) were observed at $\delta$ 3.18 (q, 4H), 5.16 (s, 2H), 5.18 (s, 2H), 5.29 (s, 2H), and 7.28 (s, 4H). The $^{13}C$ ($CDCl_3$) NMR spectrum exhibited signals at 21.1, 56.2, 105.2, 111.4, 124.9, 143.8, and 144.0 ppm. HRMS: calcd for $C_{20}H_{14}$ *m/e* 254.1096, found 254.1096.

Studies on the polymerization of **1** and **2** by silver ion are under investigation.[6]

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