

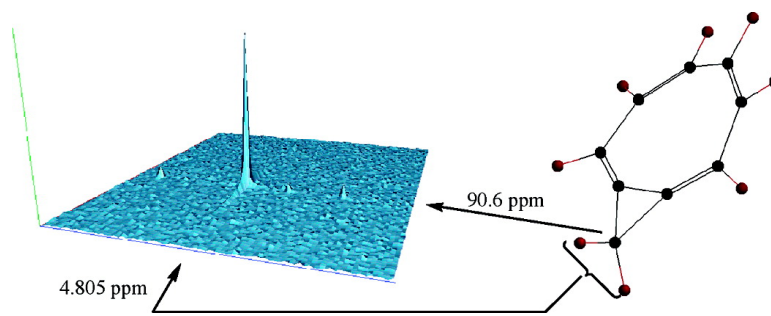
Communication

**The Second Cyclopropannulene: Cycloprop-[8]annulene**

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## The Second Cyclopropannulene: Cycloprop-[8]annulene

Matthew K. Kieseewetter, Richard C. Reiter, and Cheryl D. Stevenson\*

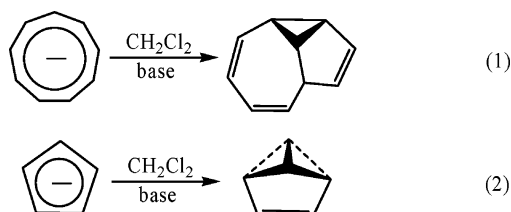
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Cycloproparenes are high-energy, highly strained hydrocarbons, in which there has been gargantuan interest resulting in a multitude of books, chapters, and reviews.<sup>1</sup> The most highly strained system in the benzocycloalkene series, cycloprop[6]annulene (**1**), is the only known member of the cyclopropannulene series. It has a strain energy greater than that of cyclopropane and was first proposed 116 years ago.<sup>2</sup> In 1963, it was predicted to have at least a transient existence, despite its high energy.<sup>3</sup> Indeed, the diatropic (aromatic) nature of the very malodiferous (to the extent that extreme caution is warranted)<sup>3</sup> cycloprop[6]annulene allowed for its isolation<sup>4</sup> and analysis of its <sup>1</sup>H NMR spectrum, which exhibits AA'BB' multiplets at  $\delta$  7.749 and 7.189.<sup>5</sup>

Despite the reactive nature of **1** (e.g. it is 45 kcal/mol more acidic than is cyclopropene), we anticipated that the cycloprop[8]annulene (**2**) might have an observable existence. It would represent the only other known member of the cyclopropannulenes. Undoubtedly, the reaction of "chlorocarbene" with [8]annulyne has led to the formation of the anion radical of cycloprop[8]annulene, which can be reoxidized to the neutral molecule.

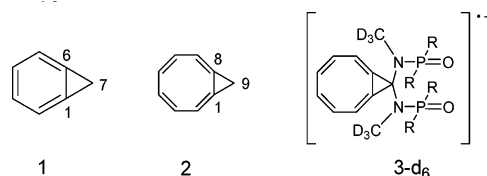
The reactions of "chlorocarbene", produced by the action of a strong base on methylene chloride,<sup>6</sup> with olefinic anions has provided a plethora of exciting compounds.<sup>7</sup> For example, Katz and co-workers<sup>7b,8</sup> used it to synthesize both benzvalene, and isobulvalene, reactions 1 and 2.



We were aware of the formation of homo[8]annulene ([6.1.0]-cyclononatriene) via the addition of the cyclooctatetraene dianion to methylene chloride.<sup>9</sup> Spurred by our successful formation of [8]-annulyne,<sup>10</sup> we reacted (at 0 °C) a mixture of CH<sub>2</sub>Cl<sub>2</sub> and monobromo[8]annulene (C<sub>8</sub>H<sub>7</sub>Br), under high-vacuum conditions, with potassium *tert*-butoxide in hexamethylphosphoramide (HMPA).<sup>11</sup> Subsequent exposure to potassium metal yields a solution that exhibits an EPR signal of an anion radical exhibiting resonances from two <sup>31</sup>P's ( $a_P = 23.26$  G), two <sup>14</sup>N's ( $a_N = 1.41$  G), six H's ( $a_H = 1.41$  G), and two groups of three H's ( $a_H = 0.36$  and 0.18 G), Figure 1.

While clearly indicating that this anion radical is a condensation product involving the solvent (the only source of nitrogen and phosphorus), the EPR signal does not suggest proton assignments. Since HMPA is well-known to attack certain anion radicals, while losing a methyl group and leaving a condensation product with a bond between the nitrogen and the attacked carbon,<sup>12</sup> we tentatively assigned the strong EPR signal to **3** [R = N(CH<sub>3</sub>)<sub>2</sub>].

Repeating the experiment in perdeuterated HMPA reveals that the two groups of three protons are methyl groups from the solvent,

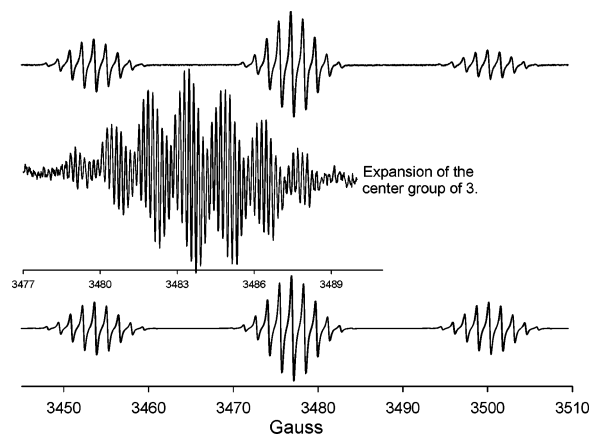


as the splittings of 0.36 and 0.18 G collapse within the line width, Figure 1. If **3** truly is responsible for the EPR spectrum, a large hyperfine splitting should result from a <sup>13</sup>C at the nine position. Accordingly, the reaction sequence was repeated with <sup>13</sup>CH<sub>2</sub>Cl<sub>2</sub>. This experiment resulted in an HMPA solution yielding the original EPR signal but with a 10.67 G hyperfine splitting from a single <sup>13</sup>C nucleus.

The K<sup>+</sup> ion is known to interact with the p<sub>x</sub> orbitals of the anion radical of [8]annulyne (**4**), even in HMPA.<sup>13</sup> The K<sup>+</sup> ion appears to guide the attack of the CHCl<sub>2</sub> anion (prior to loss of Cl<sup>-</sup> and formation of the "chlorocarbene") to the triple bond, Scheme 1.

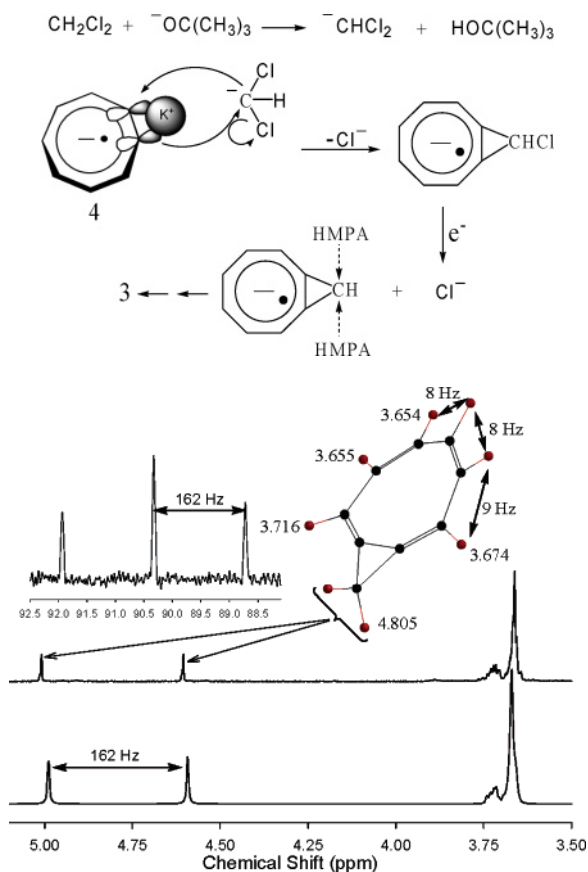
A complex analogous to **4** does not form with Na<sup>+</sup> because it is too small to overlap simultaneously with both p<sub>x</sub> orbitals.<sup>13</sup> Indeed, no trace of **3** can be observed when sodium serves as the reducing metal and sodium *tert*-butoxide serves as the dehydrohalogenating agent, as should be the case if Scheme 1 is correct.

Carrying out the reaction sequence in tetrahydrofuran (THF), as opposed to HMPA, eliminates attack by the solvent and leads to the cycloprop[8]annulene anion radical, which gives only a very weak EPR signal. The very weak signal is presumably due to favorable disproportionation, as in the case of [8]annulene itself.<sup>14</sup> However, subsequent quenching of the anion radical/dianion with I<sub>2</sub> followed by the addition of a water sodium thiosulfate (to reduce the excess iodine) solution and extraction with pentane leads to **2**.



**Figure 1.** (Upper) X-band EPR spectrum of **3-d<sub>6</sub>** in HMPA-*d*<sub>18</sub> at ambient temperature. Note that the signal, though strong, is decaying during the 10 min. scan. (Inset) Expanded view of the center group of **3** (with the reaction carried out in HMPA-*h*<sub>18</sub>). (Lower) Computer-generated simulation using an  $a_H$  of 1.41 for six H's, an  $a_N$  of 1.41 for two N's, and an  $a_P$  of 23.3 for two P's. The deuterium splittings are unresolved as they are over 6 times smaller than 0.36 and 0.18 G, the  $a_H$ 's observed in the inset.

Scheme 1

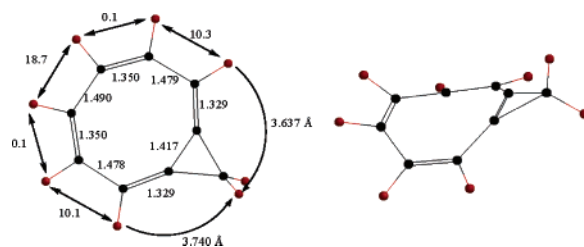


**Figure 2.** (Upper) 400 MHz  $^1\text{H}$  NMR spectrum of  $9\text{-}^{13}\text{C}$ -cycloprop[8]-annulene. (Inset)  $^{13}\text{C}$  NMR of the number 9 carbon. (Lower) Computer simulation using the  $\delta$ 's and the  $J_{\text{H-H}}$ 's shown. The  $^4J_{\text{H-H}}$  involving the pseudo-ortho protons, which are not magnetically equivalent, is 2.5 Hz. The morphology of the small multiplet is very dependent upon several very small four-bond  $J$ 's.

Upon  $^1\text{H}$  NMR analysis, the protons on carbon 9 reveal a downfield singlet at  $\delta$  4.81, signifying that the bond order between carbons 1 and 8 (within the cyclopropyl moiety) is close to unity. The analogous protons in cyclopropene appear at  $\delta$  0.93,<sup>15</sup> and those in cycloprop[6]annulene appear at  $\delta$  3.11.<sup>5</sup> The 4.81 ppm shift was verified by synthesizing  $9\text{-}^{13}\text{C}$ -cycloprop[8]annulene (from  $^{13}\text{CH}_2\text{-Cl}_2$  and [8]annulyne in THF). The NMR of the  $^{13}\text{C}$ -substituted material reveals a doublet at  $\delta$  4.81 with a 162 Hz  $J_{\text{C-H}}$ , Figure 2. As expected,  $^{13}\text{C}$  NMR shows the number 9 carbon, which appears at  $\delta$  90.4, split into a 162 Hz triplet. The assignment is confirmed via the HETCOR pulse sequence.

Surprisingly, the protons on the eight-membered ring appear in the 3.6–3.7 ppm region, as opposed to those of [8]annulene at  $\delta$  5.68,<sup>16</sup> suggesting that there is some paratropic ring current in **2**. Indeed, B3LYP/6-31G\* calculations (Figure 3) indicate that **2** is much more planar than is [8]annulene and that the structure with external (relative to the three-membered ring) double bonds is more stable than that with a cyclopropenyl moiety.

It has taken over 40 years to discover that putrescence is not common to all cyclopropannulenes; cycloprop[8]annulene has a



**Figure 3.** (Left) B3LYP/6-31G\* calculated structure of **2**. The predicted dihedral angles are given in degrees (double-headed arrows to H's) for H–C–C–H's in question. The C–C distances are given in Å. Curved arrows indicate H...H distances. (Right) Unobserved high-energy isomer.

weak, sweet olefinic odor. The strain, electronic, and magnetic properties of the other cyclopropannulenes, possibly available from “chlorocarbene” and the respective annulyne, will be of major interest. The possibility exists that cycloprop[12]annulene and cycloprop[16]annulene will also possess some degree of paratropic ring current and, perhaps, a pleasant bouquet as well.

**Acknowledgment.** We thank the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society for support.

**Supporting Information Available:** Experimental details and EPR of  $^{13}\text{C}$ -labeled **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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