

# Hydrocarbons with Carbon Frameworks Represented on the Buckminsterfullerene Surface: Indeno[7,7a,1,2,3-*lmno*]-1,12-ethenochrysene

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The excitement over the discovery of buckminsterfullerene and other carbon cages<sup>1</sup> has further enhanced the novelty of aromatic hydrocarbons with curved surfaces whose carbon frameworks can be identified on the C<sub>60</sub> surface. Corannulene (1) is the simplest example of such a hydrocarbon, and although it has been known for many years,<sup>2</sup> it was relatively inaccessible until the recent discovery of a new synthetic route.<sup>3</sup> The critical step in the synthesis (Scheme 1, eq 1) is a double ring closure accomplished by flash vacuum pyrolysis (FVP). More recently, we have employed the same method to synthesize the first semibuckminsterfullerene **2** (Scheme 1, eq 2).<sup>4</sup>

This synthetic procedure is an especially good route to curved surface aromatics since the high temperature employed produces considerable stretching and bending that facilitates ring closure to produce these strained arrangements. We were interested in testing the general utility of this method by examining a case with internal competition between ring closure to form either planar or curved products. Structure **4** represents such a case and indeed all three products, **5**–**7**, have carbon frameworks represented on the buckminsterfullerene surface; however, **5** and **7** are planar while **6** is curved.

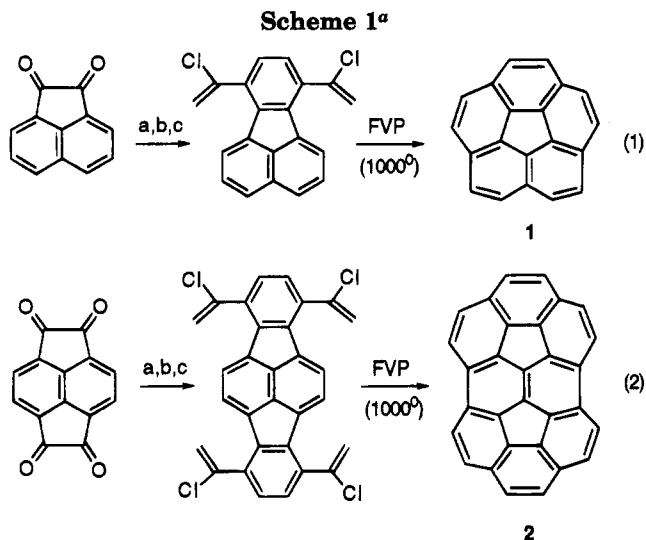
The pyrolysis of **4** proceeded very smoothly and in high yield to give a single product shown to be C<sub>24</sub>H<sub>12</sub> by mass spectroscopy. However, the <sup>1</sup>H and <sup>13</sup>C NMR spectra were more complicated than expected for either **6** or **7** since the greater symmetry of these latter structures should produce considerable simplification. Ultimately, dark brown crystals were obtained by recrystallization of the product from toluene, and the structure proof for **5** was unequivocally confirmed by X-ray crystallography.<sup>5</sup>

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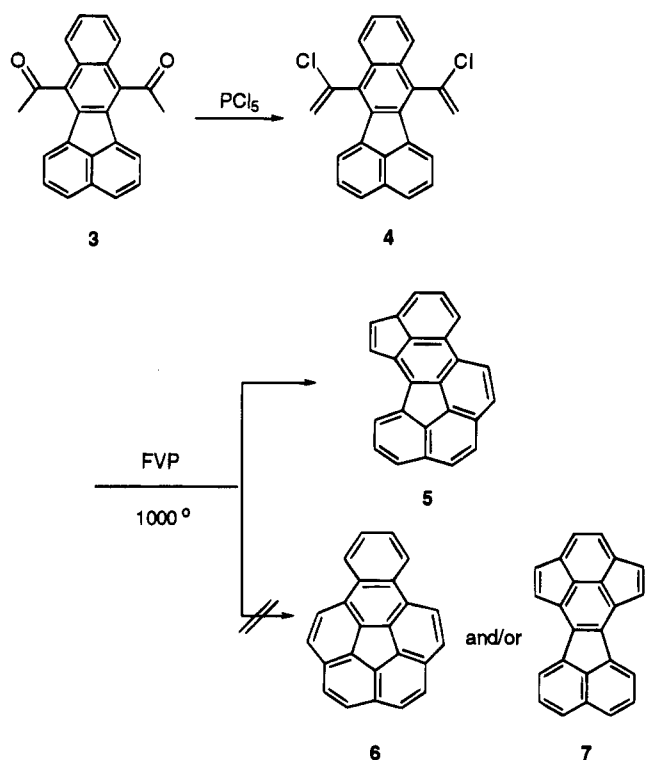
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<sup>a</sup> Key: (a) 2,4,6-heptanetrione, Et<sub>3</sub>N; (b) norbornadiene; (c) PCl<sub>5</sub>.



Hence, we may conclude that, even at high temperatures, there is a dominating preference for the formation of planar over curved products, at least when the planar product is not excessively strained.

## Experimental Section

**General Procedures.** <sup>1</sup>H (250.13 MHz) and <sup>13</sup>C (62.90 MHz) NMR spectra were recorded in CDCl<sub>3</sub>. Mass spectra were

(5) The crystal structure was determined using intensity data collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Cu Kα radiation. Crystal data: C<sub>24</sub>H<sub>12</sub>, monoclinic space group P2<sub>1</sub>/c; *a* = 4.8014(3) Å, *b* = 13.539(2) Å, *c* = 22.091(1) Å, β = 91.318(6)°, *V* = 1435.7(4) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.389 g cm<sup>-3</sup>, μ(Cu Kα) = 5.645 cm<sup>-1</sup>, *R* = 0.046, *R<sub>w</sub>* = 0.051 for 2024 observed data having *I* > 3σ(*I*). Hydrogen atoms were located from the difference map and refined isotropically. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

obtained by GC-MS. Melting points are uncorrected. The flash vacuum pyrolysis apparatus was purchased from Kontes Glass, Inc. The sample is dissolved in  $\text{CH}_2\text{Cl}_2$  and transferred to a small glass boat filled with a glass wool. The solvent is evaporated and the boat placed in the inlet chamber wrapped with a heating mantle that allows sublimation of the substrate under vacuum and a small flow of nitrogen. The pyrolysate condenses on the side arm of the quartz tube cooled with dry ice and acetone.

**7,10-Diacetylbenzo[*k*]fluoranthene (3).** To a boiling solution of 7,9-diacetyl-8-oxo-8H-cyclopent[*a*]acenaphthylene<sup>6</sup> (288 mg, 1 mmol) in anhyd DME (20 mL) were added dropwise over a period of 2 h solutions of anthranilic acid (685 mg, 5 mmol) in DME (20 mL) and isopentyl nitrite (860 mg, 7.4 mmol) in DME simultaneously from two dropping funnels. The mixture was stirred at reflux for another 1 h. DME was removed under reduced pressure and the resulting mixture extracted with  $\text{CH}_2\text{Cl}_2$ , washed with water, and dried. Flash chromatography with hexane/ $\text{CH}_2\text{Cl}_2$  (1:3) gave 317 mg (95%) of a pale yellow solid: mp 249–250 °C (from EtOH);  $^1\text{H NMR}$   $\delta$  7.91(d, 2H), 7.84–7.78 (m, 4H), 7.69–7.57 (m, 4H), 2.89 (s, 6H);  $^{13}\text{C NMR}$   $\delta$  206.60, 135.28, 135.16, 133.68, 131.48, 130.43, 128.28, 127.27 (two overlapping peaks based on intensity), 125.20, 121.89, 32.48; MS  $m/z$  336 ( $\text{M}^+$ , 73). Anal. Calcd for  $\text{C}_{24}\text{H}_{16}\text{O}_2$ : C, 85.69; H, 4.79. Found: C, 85.27; H, 4.61.

**7,10-Bis(1-chloroethenyl)benzo[*k*]fluoranthene (4).** A 490 mg (1.46 mmol) sample of **3** and 1.88 g (9.0 mmol) of  $\text{PCl}_5$  in 10 mL of toluene were refluxed for 48 h. After that time the mixture was poured into ice, the organic layer was washed with

water and sodium carbonate solution and dried, and solvent was evaporated. The residue was chromatographed on silica gel using hexane as an eluant to afford 353 mg (65%) of light yellow **4**: mp 181–182 °C (from EtOH);  $^1\text{H NMR}$   $\delta$  8.36 (d, 2H), 8.22 (dd, 2H), 7.91 (d, 2H), 7.73–7.61 (m, 4H), 6.20 (s, 2H), 5.78 (d, 2H);  $^{13}\text{C NMR}$   $\delta$  135.80, 135.68, 134.68, 131.78, 130.74, 130.31, 128.22, 127.00, 126.95, 125.73, 123.34, 119.61, 119.51; MS  $m/z$  372 ( $\text{M}^+$ , 34). Anal. Calcd for  $\text{C}_{24}\text{H}_{14}\text{Cl}_2$ : C, 77.22; H, 3.78. Found: C, 77.01; H, 3.69.

**Indeno[7,7a,1,2,3-*lmno*]-1,12-ethenochrysene (5).** A 372 mg (1 mmol) sample of **4** was pyrolyzed in four batches at 1000 °C under a slow bleed of nitrogen and 1.5 mmHg of pressure as described in the General Procedures. After each run (1–1.5 h), the pyrolysate was washed out of the elbow of the tube and cold trap with  $\text{CH}_2\text{Cl}_2$ . The crude material (225 mg) which is essentially a single product by GCMS was purified on silica gel with cyclohexane to give 195 mg (65 %) of dark brown solid **5**: mp 214–215 °C (from toluene);  $^1\text{H NMR}$   $\delta$  8.48 (d, 1H), 8.39 (d, 1H), 8.21 (d, 1H), 8.04 (d, 1H), 7.96–7.93 (m, 3H), 7.76–7.66 (m, 3H), 7.48 (d, 1H), 7.39 (d, 1H);  $^{13}\text{C NMR}$   $\delta$  134.81, 128.20, 128.10, 126.92, 126.10, 126.04, 125.35, 125.07, 124.31, 123.31, 122.83, 122.62 (all CH by DEPT experiment), 158.29, 140.09, 136.51, 136.25, 135.54, 133.48, 131.58 (quat); MS  $m/z$  300 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{24}\text{H}_{12}$ : C, 95.97; H, 4.03. Found: C, 95.64; H, 3.96.

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