

$\epsilon$  rose to  $7.2 \times 10^{-2} \text{ W kg}^{-1}$ . Application of eq 3 gave  $t_D = 0.28 \text{ s}$  (75 rpm) and  $0.035 \text{ s}$  (300 rpm). Measured yields of R were 84% (75 rpm) and 98.1% (300 rpm).

(b) pH 7. The 1-naphthol solution (500 mL) was buffered ( $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ ) to pH 7.0, and 20 mL of B was added as before. The value of  $t_R$  rose to 0.14 s, whereas  $t_D$  was unchanged. Measured yields were 99.4% (75 rpm) and  $\approx 99.9\%$  (300 rpm).

(c) pH 2-10. Acidic B (20 mL, pH 2) was first added rapidly to 500 mL of unbuffered A solution. Then 20 mL of  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  buffer solution, pH 10, was added over 4 min so that coupling could proceed. (In the context of homogeneous catalysis, this is equivalent to initiating reaction by addition of catalyst.) At 75 and 300 rpm, yields of R were  $\approx 99.9\%$ .

In all experiments, the total B content of R and S, namely,  $c_R + 2c_S$ , was within  $\pm 1\%$  of the quantity of diazonium ion added. These good mass balances indicate satisfactory experiments and conformance with eq 1 and 2.

Registry No. A, 90-15-3; B, 305-80-6.

### Synthesis of Hexacyclo[6.5.1.0<sup>2,7</sup>.0<sup>3,11</sup>.0<sup>4,9</sup>.0<sup>10,14</sup>]tetradeca-5,12-diene<sup>1</sup>

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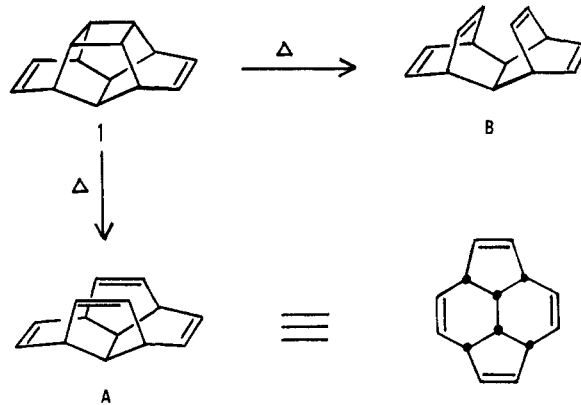
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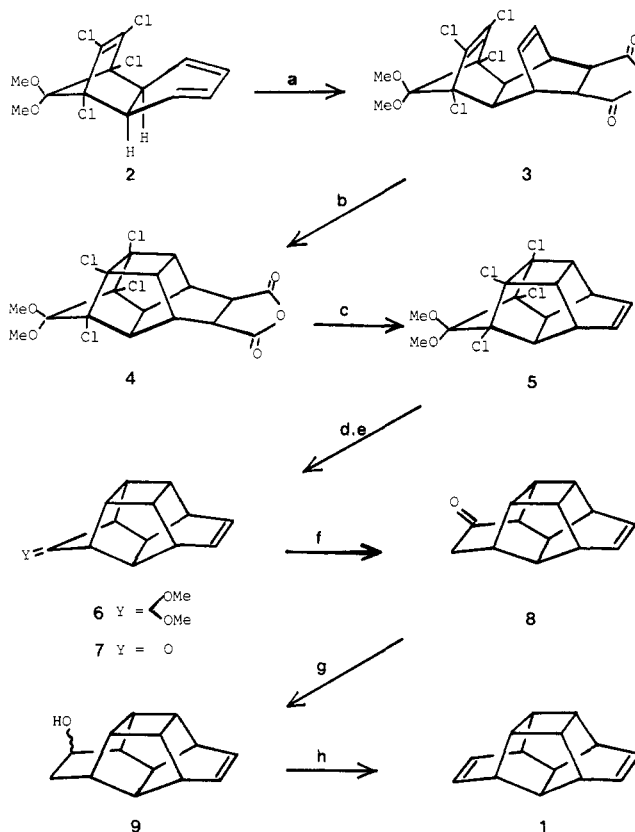
Polycyclic cage compounds that possess novel molecular frameworks have attracted considerable interest among organic chemists for many decades.<sup>2</sup> Recent attention to 1,3-bishomopentaprismane systems<sup>3,4</sup> and their applications to the construction of tetraquinane derivatives via thermal cleavage of the inherent cyclobutane ring<sup>4</sup> prompts us to report a new route to the title compound (1).<sup>4d</sup> Compound 1 is a  $C_{2v}$ -symmetric  $(\text{CH})_{14}$ -diene, bearing structural resemblance to 1,3-bishomopentaprismane.<sup>5</sup> As shown in Scheme I, this diene holds promise as a potential precursor to hitherto unknown 1,8:4,5-diethenonaphthalene A and/or 1,4:5,8-diethenonaphthalene B, since its strained cyclobutane ring may likewise be thermally induced to cleave.<sup>4d</sup>

Our synthetic approach to diene 1 is outlined in Scheme II. The required *endo*-1,8,9,10-tetrachloro-11,11-dimethoxytricyclo[6.2.1.0<sup>2,7</sup>]undeca-3,5,9-triene (2) is readily accessible from the Diels-Alder cycloadduct of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene and *p*-benzoquinone in three steps.<sup>6</sup> Basically, the elaboration of bicyclic 2 into the framework of hexacyclic diene 1 consists of three

Scheme I



Scheme II<sup>a</sup>



<sup>a</sup> (a) Maleic anhydride, benzene, 80 °C, 4 h (3, 98%); (b) acetone, light, 30 h (4, 98%); (c) electrolysis,  $\text{Et}_3\text{N}$ ,  $\text{Py}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}$  (5, 60%); (d) Na, *t*-BuOH, THF, reflux, 36 h (6, 74%); (e)  $\text{H}_2\text{O}$ -THF,  $\text{TsOH}$  (catalytic amount), reflux, overnight (7, 92%); (f)  $\text{CH}_2\text{N}_2$ ,  $\text{Et}_2\text{O}$ , 0-4 °C, 2 days (8, 96%); (g)  $\text{NaBH}_4$ , MeOH, room temperature, 10 min (9, 97%); (h) benzene,  $\text{TsOH}$  (catalytic amount), azeotropic reflux, 3 days (1, 80%).

key operations: (1) the addition of an acetylene equivalent to the diene unit of 2 by a Diels-Alder reaction; (2) photocycloaddition of two suitably oriented C=C double bonds to form the hexacyclic cage skeleton; and (3) the transformation of the bicyclo[2.2.1]heptane moiety to the bicyclo[2.2.2]octane substructure by ring expansion.

Although triene 2 is more stable than the unsubstituted parent hydrocarbon<sup>7</sup> toward retro-Diels-Alder reaction to yield benzene and the respective cyclopentadiene, it does show such a tendency in solution at temperatures above 100 °C.<sup>6</sup> The decision was therefore made to employ

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maleic anhydride, the strong and readily available classic dienophile, as an acetylene equivalent. Thus, heating this reagent in a benzene solution with **2** at 80 °C afforded a single product **3** in near-quantitative yield. The syn orientation of the anhydride moiety (with respect to the C=C double bond) in the adduct **3** is assigned by expectation of an endo-type addition in accordance with the Alder rule. That the two C=C double bonds in **3** are in close proximity is a result of the approaching of the dienophile from the less hindered "outside" face of **2** and is established by its ready photocyclization to **4**.

Irradiation of an acetone solution of **3** proceeded slowly but efficiently to produce hexacyclic photoadduct **4** in quantitative yield. Direct decarboxylation of the anhydride functional group in **4** to an olefinic moiety was carried out electrolytically<sup>8</sup> and provided **5** in 60% yield with good reproducibility. Dechlorination of **5** with sodium-*tert*-butyl alcohol in tetrahydrofuran, followed by acid-catalyzed hydrolysis of the resultant **6**, furnished hexacyclo-[5.5.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>4,8</sup>.0<sup>9,13</sup>]tridec-11-en-5-one (**7**) in an overall yield of 68%. Characterization of **7** and its precursors was accomplished by analyses of elemental composition and spectral data. In particular, the inherent C<sub>s</sub> symmetry was maintained as evident from their rather simple <sup>1</sup>H NMR spectra and only seven signals for the skeletal carbon atoms in the <sup>13</sup>C NMR spectra.

With the acquisition of **7**, the expansion of the carbonyl bridge by a methylene group was now called for. This transformation (**7** → **8**) was rendered a simple matter with diazomethane as the reagent.<sup>9</sup> Upon saturation of an ethereal solution of **7** with diazomethane, the yellow color gradually faded when the solution was stored at 0–4 °C for 2 days, and a single product was formed and isolated in 96% yield. This material was characterized as a homologue of **7** by elemental analysis for C<sub>14</sub>H<sub>14</sub>O. Both the <sup>1</sup>H and <sup>13</sup>C NMR spectra clearly indicate that the symmetry element (mirror plane) intrinsic to **7** is removed, and the spectra are consistent only with the formation of ring-expanded ketone **8**. Ketone **8** was then reduced with sodium borohydride in methanol, thereby affording quantitatively a 1:1 mixture of stereoisomeric alcohols **9**. This mixture was characterized spectroscopically, and in particular, the number of carbon signals in the <sup>13</sup>C NMR spectrum corresponded well to the existence of two epimers (see Experimental Section).

The epimeric alcohols **9**, without separation, were dissolved in benzene and subjected to acid-catalyzed dehydration. The title compound **1** was thereby obtained as a colorless liquid in 80% yield (30% overall from **2**). Characterization of **1** was accomplished by analyses of mass and <sup>13</sup>C NMR spectra and was aided by comparison of its IR and proton NMR spectra with reported ones.<sup>4d</sup> The inherent C<sub>2v</sub> symmetry expected for **1** is obviously demonstrated by a four-line <sup>13</sup>C NMR spectrum.

### Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. NMR spectra were obtained on a JEOL FX-100FT and a Varian VXR-300FT spectrometer, and the chemical shifts are reported in parts per millions (δ) downfield from tetramethylsilane. Infrared (IR) spectra were recorded on a Perkin-Elmer 682 spectrophotometer. Mass spectra (MS) were taken at 12 eV on a JEOL JMS-D-100 mass spectrometer. Elemental microanalyses were performed by Analytical Center op-

erated by the Cheng-Kung University, Tainan, Taiwan.

(1α,2β,3α,6α,7β,8α,11β,12β)-3,4,5,6-Tetrachloro-13,13-dimethoxytetracyclo[6.2.2.1<sup>3,6</sup>.0<sup>2,7</sup>]trideca-4,9-diene-11,12-dicarboxylic Anhydride (**3**). A solution of **2** (19.0 g, 0.056 mol) and maleic anhydride (5.7 g, 0.058 mol) in dry benzene (100 mL) was refluxed under nitrogen, and the reaction was monitored by TLC analysis. When **2** had disappeared (4 h), most of the solvent was removed under reduced pressure and the resulting solid residue was collected by suction filtration to give pure compound **3** (21.5 g, 88%). The filtrate was concentrated and chromatographed on silica gel (1:3 ethyl acetate–hexane eluent) to afford an additional crop of **3** (2.5 g, 10%). The total yields were constantly above 95%. An analytical sample was obtained by recrystallization from ethyl acetate–hexane (1:1) as a colorless crystalline solid: mp 244–245 °C; IR (KBr) 3035 (w), 1860 (sh), 1845 (s), 1775 (s), 1610 (m), 1195 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 6.12 (center of an ABX-like system, *J* = 4.4 and 3.2 Hz, 2 H), 3.58 (s, 3 H), 3.49 (s, 3 H), 3.45 (m, 2 H), 3.18 (t, *J* = 1.5 Hz, 2 H), and 2.75 (br s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 170.50 (s), 127.97 (d), 127.61 (s), 113.85 (s), 76.93 (s), 52.91 (q), 51.68 (q), 49.22 (d), 45.70 (d), and 31.61 (d); MS, *m/e* (relative intensity) 442 (3), 440 (6), 438 (5) [M<sup>+</sup>], 407 (32), 405 (96), 403 (100), 257 (18), 255 (59), 253 (61), 78 (3).

Anal. Calcd for C<sub>17</sub>H<sub>14</sub>Cl<sub>4</sub>O<sub>5</sub>: C, 46.37; H, 3.21; Cl, 32.24. Found: C, 46.40; H, 3.26; Cl, 32.15.

(1α,11α,12α)-4,6,7,8-Tetrachloro-5,5-dimethoxyhexacyclo[5.5.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>4,8</sup>.0<sup>9,13</sup>]tridecane-11,12-dicarboxylic Anhydride (**4**). A solution of anhydride **3** (22.0 g, 0.05 mol) in acetone (400 mL) was irradiated with a 450-W Hanovia medium-pressure Hg lamp housed in a quartz well. During irradiation, a slow stream of nitrogen was bubbled through the solution and the progress of reaction was followed by NMR analysis. When the conversion was complete (30 h), most of the acetone was evaporated and the precipitated product was collected by suction filtration to give caged anhydride **4** (20.0 g, 91%) as a colorless crystalline solid. The filtrate was concentrated and chromatographed on silica gel (1:3 ethyl acetate–hexane eluent) to yield an additional portion of **4** (1.7 g, total yield 98%). Recrystallization from ethyl acetate–hexane (1:1) afforded an analytical sample: mp 296–297 °C; IR (KBr) 1860 (s), 1845 (sh), 1775 (s), 1235 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 3.67 (s, 3 H), 3.59 (s, 3 H), 3.29 (t, *J* = 1.7 Hz, 2 H), 2.89 (m, 2 H), and 2.87 (m, 4 H); MS, *m/e* (relative intensity) 442 (2), 440 (4), 438 (3) [M<sup>+</sup>], 407 (31), 405 (96), 403 (100).

Anal. Calcd for C<sub>17</sub>H<sub>14</sub>Cl<sub>4</sub>O<sub>5</sub>: C, 46.37; H, 3.21; Cl, 32.24. Found: C, 46.43; H, 3.23; Cl, 32.03.

4,6,7,8-Tetrachloro-5,5-dimethoxyhexacyclo[5.5.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>4,8</sup>.0<sup>9,13</sup>]tridec-11-ene (**5**). The electrolysis was carried out in a 250-mL beaker covered with a three-hole cardboard into which a pair of platinum plates (1.5 cm on an edge) and a nitrogen inlet tube were immersed. The platinum electrodes were respectively connected to the positive and negative terminals of a power supply. Caged anhydride **4** (3.0 g, 0.068 mol) was dissolved in a mixture of triethylamine (3 mL) and pyridine (10 mL). When a clear solution was obtained, water (10 mL) and acetonitrile (200 mL) were subsequently added. The reaction mixture was stirred and flushed with nitrogen, and the power was turned on. The temperature of the reaction mixture was monitored with a water bath. The initial voltage was 60 V, and the current was 200 mA. During the reaction period, carbon dioxide was generated at the anode and the electric current gradually decreased. When gas ceased to evolve at the anode followed by a drop in current (usually to 25 mA), the reaction was judged complete. The electrolysis time was usually 4 h per gram of the anhydride. The reaction mixture was worked up by removing solvents in vacuo to a total of about 10 mL, followed by dilution with water (25 mL) and extraction with ethyl acetate (2 × 25 mL). The extracts were combined, washed with 10% HCl solution (25 mL), dried over sodium sulfate, and filtered. Removal of solvent left a brown residue, which was chromatographed on silica gel (1:10 ethyl acetate–hexane eluent) to afford olefin **5** (1.5 g, 60%).

An analytically pure sample of **5** was obtained by recrystallization from ethyl acetate as a colorless crystalline solid: mp 117–118 °C; IR (KBr) 3040 (w), 1625 (w), 1230 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 6.26 (center of an ABX-like system, *J* = 4.9 and 3.2 Hz, 2 H), 3.63 (s, 3 H), 3.59 (s, 3 H), 3.40 (m, 2 H), and 2.57 (m,

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4 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  129.61 (d), 106.34 (s), 77.69 (s), 76.76 (s), 52.56 (d), 51.56 (q), 51.09 (q), 49.33 (d), and 36.50 (d); MS,  $m/e$  (relative intensity) 370 (9), 368 (16), 366 (15) [ $\text{M}^+$ ], 337 (21), 335 (38), 333 (94), 331 (100).

Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{Cl}_4\text{O}_2$ : C, 48.92; H, 3.83; Cl, 38.54. Found: C, 48.84; H, 3.84; Cl, 38.37.

**5,5-Dimethoxyhexacyclo[5.5.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>4,8</sup>.0<sup>9,13</sup>]tridec-11-ene (6).** Into a 100-mL reaction flask were placed, in order, compound 5 (3.0 g, 0.008 mol), dry tetrahydrofuran (60 mL), *tert*-butyl alcohol (6.0 g, 0.008 mol), and sodium (5.4 g, 0.235 g-atom) chopped into 5-mm cubes. The mixture was vigorously stirred and refluxed under a nitrogen atmosphere for 36 h, then cooled to room temperature, and filtered to remove unreacted sodium. The filtrate was poured into ice water (20 mL) and extracted with ether (2  $\times$  30 mL). The organic phase was washed with brine (30 mL), dried, and concentrated. The resulting pale brown residue was purified via flash chromatography on silica gel (1:20 ethyl acetate-hexane eluent) and recrystallization from the same system of solvents to furnish pure 6 (1.4 g, 74%) as a colorless crystalline solid: mp 74-75 °C; IR (KBr) 3015 (w), 1615 (w), 1060  $\text{cm}^{-1}$  (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.22 (center of an ABX-like system,  $J = 4.9$  and 3.1 Hz, 2 H), 3.30 (s, 3 H), 3.23 (s, 3 H), 2.84 (m, 2 H), 2.64 (m, 2 H), 2.30 (m, 2 H), 2.26 (m, 2 H), and 2.20 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  130.53 (d), 117.77 (s), 50.89 (q), 50.79 (q), 46.54 (d), 45.94 (d), 40.66 (d), 40.49 (d), and 40.39 (d); MS,  $m/e$  (relative intensity) 230 (100) [ $\text{M}^+$ ], 199 (37) [ $\text{M}^+ - \text{OCH}_3$ ], 152 (32), 121 (26), 74 (31).

Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_2$ : C, 78.22; H, 7.88. Found: C, 78.33; H, 7.87.

**Hexacyclo[5.5.1.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>4,8</sup>.0<sup>9,13</sup>]tridec-11-en-5-one (7).** To a solution of acetal 6 (1.0 g, 0.0043 mol) in tetrahydrofuran (30 mL) containing water (20 mL) was added a catalytic amount of *p*-toluenesulfonic acid. The reaction mixture was refluxed overnight and then extracted with ether (2  $\times$  25 mL). The extracts were washed with water (20 mL) and brine (20 mL) prior to drying and filtration. Concentration and flash chromatography on silica gel (1:8 ethyl acetate-hexane eluent) of the resulting residue afforded pure ketone 7 (0.74 g, 92%), which was crystallized from ethyl acetate-hexane as a colorless crystalline solid: mp 103-104 °C; IR (KBr) 3015 (w), 1760 (s), 1735  $\text{cm}^{-1}$  (sh);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.29 (center of an ABX-like system,  $J = 4.9$  and 3.2 Hz, 2 H), 3.09 (m, 2 H), 2.78 (m, 2 H), 2.46 (m, 2 H), 2.31 (m, 2 H), and 2.11 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  215.06 (s), 129.97 (d), 46.47 (d), 42.78 (d), 42.25 (d), 41.39 (d), and 36.84 (d); MS,  $m/e$  (relative intensity) 184 (100) [ $\text{M}^+$ ], 156 (18) [ $\text{M}^+ - \text{CO}$ ], 141 (4), 106 (6), 91 (7), 78 (74).

Anal. Calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$ : C, 84.74; H, 6.57. Found: C, 84.83; H, 6.61.

**Hexacyclo[6.5.1.0<sup>2,7</sup>.0<sup>3,11</sup>.0<sup>4,9</sup>.0<sup>10,14</sup>]tetradec-12-en-5-one (8).** An ethereal solution (30 mL) of ketone 7 (670 mg, 3.6 mmol) was saturated with freshly generated diazomethane at 0 °C. The mixture was then allowed to stand in the dark in a refrigerator (ca. 4 °C) for 2 days. The pale yellow color of the solution disappeared almost completely at this point. The solution was concentrated to leave an off-white solid, which was purified via flash chromatography on silica gel (1:8 ethyl acetate-hexane eluent) to afford pure enone 8 (690 mg, 96%). Recrystallization from ethyl acetate-hexane gave an analytical sample as a colorless crystalline solid: mp 90-91 °C; IR (KBr) 3035 (w), 1735 (s), 1625  $\text{cm}^{-1}$  (w);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.26 (m, 2 H), 2.93 (m, 1 H), 2.69 (m, 2 H), 2.62 (m, 1 H), 2.45 (m, 1 H), 2.36 (m, 2 H), 2.22 (m, 2 H), 2.12 (m, 2 H), and 1.92 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  216.89 (s), 131.44 (d), 129.48 (d), 50.71 (d), 42.54 (d), 40.82 (d), 40.54 (d), 40.34 (d), 39.89 (d), 39.62 (d), 38.73 (d), 37.34 (t), 36.78 (d), and 35.92 (d); MS,  $m/e$  (relative intensity) 198 (100) [ $\text{M}^+$ ], 156 (31) [ $\text{M}^+ - \text{H}_2\text{C}=\text{C}=\text{O}$ ], 154 (69), 131 (30), 118 (14), 78 (30).

Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}$ : C, 84.80; H, 7.12. Found: C, 84.65; H, 7.18.

**Hexacyclo[6.5.1.0<sup>2,7</sup>.0<sup>3,11</sup>.0<sup>4,9</sup>.0<sup>10,14</sup>]tetradec-12-en-5-ol (9).** To a stirred solution of 8 (500 mg, 2.5 mmol) in methanol (25 mL) was added sodium borohydride (500 mg, 12.5 mmol) in three portions in a period of 3 min. The reaction mixture was stirred at room temperature, and the progress of the reaction was monitored by TLC analysis. When ketone 8 had disappeared (ca. 10 min), a solution of 10% HCl (10 mL) was added. The bulk of the methanol was removed under reduced pressure, and the

product was extracted into ether. The ethereal solution was washed with 5% sodium bicarbonate solution and brine, dried, and evaporated to leave crude 9 (510 mg) as a colorless solid. Flash chromatography on silica gel (1:10 ethyl acetate-hexane as eluent) furnished a 1:1 mixture of epimeric alcohols 9 (490 mg, 97%), which was recrystallized from the same system of solvents to give an analytical sample as a colorless crystalline solid: mp 80-82 °C; IR (KBr) 3270 (s, br), 3020 (w), 1625 (w), 1100 (s), 1050  $\text{cm}^{-1}$  (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.26 (m, 4 H, olefinic protons), 4.22 (m, 1 H, HCO), 3.95 (m, 1 H, HCO), 2.79 (m, 1 H), 2.52 (m, 6 H), 2.45 (m, 1 H), 2.24 (m, 4 H), 1.96 (m, 2 H), and 1.82-1.28 (m, 12 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  131.21 (d), 130.94 (d), 130.63 (d), 130.44 (d), 65.59 (d), 65.37 (d), 41.47 (d), 41.27 (d), 41.21 (d), 40.96 (d), 40.77 (d), 40.58 (d, 2 C), 40.34 (d), 40.32 (d), 39.93 (d), 39.79 (d), 39.70 (d), 39.18 (d), 37.40 (d), 36.92 (d), 36.71 (d), 35.56 (d), 33.54 (d), 33.24 (d), 32.32 (d), 31.17 (t), 30.73 (t); MS,  $m/e$  (relative intensity) 200 (100) [ $\text{M}^+$ ], 182 (33) [ $\text{M}^+ - \text{H}_2\text{O}$ ], 167 (8), 156 (19), 141 (9), 133 (7), 104 (11), 91 (15), 80 (23), 78 (12).

Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}$ : C, 83.95; H, 8.06. Found: C, 83.85; H, 8.17.

**Hexacyclo[6.5.1.0<sup>2,7</sup>.0<sup>3,11</sup>.0<sup>4,9</sup>.0<sup>10,14</sup>]tetradeca-5,12-diene (1).** A catalytic amount of *p*-toluenesulfonic acid was added to a solution of 9 (100 mg, 0.5 mmol) in dry benzene (30 mL), and the reaction mixture was heated at reflux temperature in an atmosphere of nitrogen for 3 days under a Dean-Stark trap. Most of the benzene was then removed in vacuo, and the residue was purified via flash chromatography on silica gel (hexane eluent) to afford diene 1 (73 mg, 80%) as a colorless liquid: IR (film) 3030 (m), 1620 (m), 1380 (m), 1320 (m), 830 (m), 685  $\text{cm}^{-1}$  (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  6.27 (center of an ABX-like system,  $J = 4.8$  and 3.2 Hz, 4 H, olefinic protons), 2.53 (br s, 4 H, allylic bridgehead protons), 2.28 (m, 4 H, cyclobutane methine protons), and 1.60 (m, 2 H, bridgehead methine protons);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  131.72 (d), 44.10 (d), 39.22 (d), and 38.79 (d); MS,  $m/e$  (relative intensity) 182 (100) [ $\text{M}^+$ ], 167 (11), 154 (4), 141 (5), 104 (60), 91 (30).

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### Synthesis of 2',3'-Dideoxyuridine via Deoxygenation of 2',3'-O-(Methoxymethylene)uridine

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Reductive deoxygenation of a vicinal diols moiety of a nucleoside is an attractive synthetic route to 2',3'-dideoxynucleosides, which are physiologically important<sup>1</sup> and play an important role in protecting cells against the cytopathic effect of HIV.<sup>2</sup> In fact, the syntheses of dideoxynucleosides from ribonucleosides have been studied extensively. For example, 2'-O-acetyl-3'-bromo-3'-deoxynucleoside derivatives have been used as precursors of

(1) Recently, 2',3'-dideoxynucleosides, such as 2',3'-dideoxycytidine, 2',3'-dideoxyadenosine, and 2',3'-dideoxyinosine, were found to be effective against AIDS (acquired immune deficiency syndrome). (a) Mitsuya, H.; Weinhold, K. J.; Ufrmann, P. A.; St. Clair, M. H.; Lehrman, S. N.; Gallo, R. C.; Bolognesi, D.; Barry, D. W.; Broder, S. *Proc. Natl. Acad. Sci. U.S.A.* 1985, 82, 7096. (b) Mitsuya, H.; Broder, S. *Ibid.* 1986, 83, 1911. (c) Kim, C.; Marquez, V. E.; Broder, S.; Mitsuya, H.; Driscoll, J. S. *J. Med. Chem.* 1987, 30, 862. (d) Herdewijn, P.; Balzarini, J.; Clercq, E. D.; Pawels, R.; Baba, M.; Broder, S. *Ibid.* 1987, 30, 1270.

(2) Human immunodeficiency virus, which causes AIDS. For instance: (a) Provic, M.; Sarngadharan, M. G.; Read, E.; Gallo, R. C. *Science (Washington, D.C.)* 1984, 224, 497. (b) Broder, S.; Gallo, R. C. *Annu. Rev. Immunol.* 1985, 3, 321. (c) Wong-Staal, F.; Gallo, R. C. *Nature (London)* 1985, 317, 395.