and then the slurry was left under positive hydrogen pressure (1 atm) and stirred for 12 h at room temperature. The crude product was obtained following filtration of the reaction mixture through magnesium sulfate, subsequent rinsing of the vessel and filter cake with ethyl acetate (10 cm^3), and evaporation in vacuo. Preparative TLC (1:1 ether/hexane) afforded pure product (0.091 g, 83%). Evaporative distillation (150–160 °C, 0.020 torr) produced analytical material: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.07–7.0 (m, 3 H), 6.72 (AB, 2 H, J = 8.56 Hz), 6.67 (d, 1 H, J = 2.47 Hz), 6.48 (dd, 1 H, J_1 = 8.31 Hz, J_2 = 2.48 Hz), 5.45 (broad, 1 H), 5.16 (s, 2 H), 3.76 (s, 3 H), 3.46 (s, 3 H), 2.59 (t, 2 H, J = 7.61 Hz), 2.57 (t, 2 H, J = 7.70 Hz), 1.84 (m, 2 H); IR (neat) 3400, 2940, 1610, 1510, 1215, 1150, 1105, 825 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.55; H, 7.48.

2-[3-(4-Hydroxyphenyl)propyl]-5-methoxyphenol (Broussonin A, 1). To a stirred solution of 11 (0.091 g, 3.01 mmol) in THF (2 cm^3) and 2-propanol (2 cm^3) at room temperature was added concentrated HCl (0.4 cm^3) dropwise. The mixture was stoppered and stirred for 20 h, at which time it was poured into water (60 cm^3) and then extracted with 75 cm^3) of ether in three portions. The combined organic phases were washed with 10 cm^3 of dilute sodium bicarbonate and 50 cm^3 of brine, dried over magnesium sulfate, and then filtered, the filtrate was evaporated in vacuo to give the crude product as an oil. Preparative TLC (1:1 ether/hexane) provided pure broussonin A (1; 0.059 g, 76%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.02–6.95 (m, 3 H), 6.70 (AB, 2 H, J = 8.57 Hz), 6.41 (dd, 1 H, J_1 = 2.52 Hz, J_2 = 8.28 Hz), 6.34 (d, 1 H, J = 2.48 Hz), 5.6 (broad, 2 H), 3.69 (s, 3 H), 2.53 (m, 4 H), 1.83 (m, 2 H); ^{1}H NMR (200 MHz, acetone-d_6) δ 8.10 (br s, 1 H), 8.09 (br s, 1 H), 7.02 (AB, 2 H, J = 8.63), 6.97 (d, 1 H, J = 8.31 Hz), 6.74 (AB, 2 H, J = 8.57 Hz), 6.43 (d, 1 H, J = 2.48 Hz), 6.34 (dd, 1 H, J_1 = 2.53 Hz, J_2 = 8.25 Hz), 3.69 (s, 3 H), 2.58 (t, 2 H, J = 7.66 Hz), 2.55 (t, 2 H, J = 7.65 Hz), 1.84 (m, 2 H); IR (neat) 3380, 2930, 1615, 1510, 830 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.25; H, 7.28.

Acknowledgment. We thank Dr. Mitsuo Takasugi for his generous gift of authentic broussonin A and the Boeing Co. for their financial assistance in the purchase of the 200 MHz spectrometer.

Registry No. 1, 73731-87-0; 3, 10210-17-0; 4, 61440-45-7; 5, 68486-77-1; 6, 57234-28-3; 7, 89321-21-1; 8, 89321-22-2; 9, 89321-23-3; 10, 89321-24-4; 11, 89321-25-5.

Heptacyclo[5.5.1.1^{4,10}.0^{2,6}.0^{3,11}.0^{5,9}.0^{8,12}]tetradecane-13,14-dione: A Novel, Polycyclic Perpendobiplanar D_{2d} Diketone

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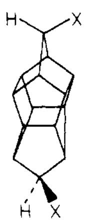
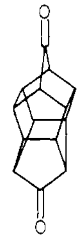
Received December 31, 1983

Since it was first reported in 1961,[1] heptacyclo[5.5.1.1^{4,10}.0^{2,6}.0^{3,11}.0^{5,9}.0^{8,12}]tetradecane (HCTD, 1) has continued to fascinate organic chemists.[2-4] Early attempts to verify its structure via single-crsytal X-ray crystallographic analysis were precluded due to crystal twinning.[1] The structure of 1 instead has been inferred by chemical methods.[2] Attempts to functionalize 1 via direct substitution of C–H bonds by using electrophilic or free-radical reagents have not been successful.[5] The 13,14-di-*tert*-butoxy derivative of 1 (i.e., 2) has been synthesized via iron carbonyl promoted cyclodimerization of 7-*tert*-butoxynorbornadiene,[6] and its structure has been confirmed via single-crystal X-ray structural analysis.[7] However, to our knowledge, no other functionalized HCTD's have been reported. We now report the synthesis of four new HCTD's (i.e., compounds 3–6).



1, X = H
2, X = O-*t*-Bu
3, X = OC(O)Ph
4, X = OC(O)(p-$C_6H_4OCH_3$)
5, X = OH



6

The following reaction sequence was employed for the synthesis of 3–6: The iron carbonyl promoted cyclodimerization[6] of 7-(benzoyloxy)norbornadiene (7) affords 3 in 15% yield along with other products. Similarly, 4 is obtained in 14% yield via iron carbonyl promoted cyclodimerization of 7-[(p-methoxybenzoyl)oxy]norbornadiene (8). Both compounds 3 and 4 can be isolated from the reaction mixture via precipitation, which occurs upon dilution of the crude reaction mixture with an equal volume of absolute ethanol. Hydrolysis of 3 was effected by refluxing in excess aqueous ethanolic KOH solution; 5 was obtained thereby in 85% yield. Oxidation of 5 with pyridinium chlorochromate in methylene chloride–dimethyl sulfoxide solution[8] afforded 6 (93%).

Compound 6, like the parent hydrocarbon (HCTD, 1), possesses unusual symmetry properties; it is one of the rare existing rigid, polycyclic organic molecules that belongs to point group D_{2d}. Compound 6 is a dendroasymmetric molecule with a perpendobiplanar structure, i.e., 6 possesses fourfold alternating axial symmetry and, in addition, it contains a C_2 rotation axis that is coincident with its major axis.[9]

Cycloreversion of 6 to 2 mol each of benzene and carbon monoxide is expected to be a highly exoergic process. However, this pericyclic reaction is forbidden to occur thermally in a concerted fashion due to the restraints imposed by orbital symmetry considerations.[10] Accordingly, the expected exothermicity of this process may well be offset by a relatively high activation energy barrier. Indeed, we find 6 to be thermally stable; it can be stored for months at ambient temperatures.

Experimental Section

Melting points are uncorrected. Proton NMR spectra were obtained with Varian EM-360 and Varian XL-300 NMR spectrometers. ^{13}C NMR spectra were recorded on an IBM/Bruker

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NR-80 NMR spectrometer. In all cases, signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained on a Beckman Model 4250 infrared spectrophotometer. Mass spectra were obtined on a Hewlett-Packard Model 5985B mass spectrometer (70 eV). Elemental microanalyses were preformed by Chemalytics, Inc., Tempe, AZ, and by Galbraith Laboratories, Inc., Knoxville, TN. 7-(Benzoyloxy)norbornadiene was used as obtained from Frinton Laboratories, Inc., Vineland, NJ, or synthesized by a literature procedure.[11]

7-[(*p*-Methoxybenzoyl)oxy]norbornadiene (8). To a two-necked flask fitted with a dropping funnel and a calcium chloride drying tube was added a solution of *p*-anisoyl chloride (10.5 g, 61.6 mmol) in dry pyridine (30 mL). 7-Norbornadienol[11] (15.67 g, 14.49 mmol) was placed in the dropping funnel and added dropwise to the stirred reaction mixture. After all of the 7-norbornadienol had been added, the drying tube was replaced by a reflux condenser and the reaction mixture was refluxed for 1 h, at which time it was allowed to cool to room temperature. Diethyl ether was added, and the resulting mixture was then extracted with 10% aqueous sodium bicarbonate solution (100 mL). The organic layer was washed successively with 10% aqueous hydrochloric acid and then with water, dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The oily residue was digested with pentane, whereupon crystallization occurred. Recrystallization of the crude product from ether–pentane mixed solvent afforded 8 (11.22 g, 75.2%) as a colorless microcrystalline solid: mp 81.5–82.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.65 (m, 2 H), 3.80 (s, 3 H), 4.8 (m, 1 H), 6.6 (m, 4 H), 6.85 (upfield half of an AA′BB′ pattern, 2 H), 7.9 (lowfield half of an AA′BB′ pattern, 2 H); IR (KBr) 1720 (m), 1620 (m), 1520 (w), 1470 (w), 1330 (m), 1290 (m), 1255 (s), 1190 (m), 1172 (m), 1104 (m), 1069 (w), 1030 (w), 1004 (m), 850 (w), 811 (m), 772 (m), 712 (m) cm^{-1}.

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.26; H, 5.69.

Reaction of 7-(Benzoyloxy)norbornadiene (7) with Iron Pentacarbonyl. To a solution of 7 (10.0 g, 47.1 mmol) in freshly distilled di-*n*-butyl ether (50 mL) under nitrogen was added a solution of iron pentacarbonyl (18.5 g, 94.4 mmol) in di-*n*-butyl ether (10 mL). The resulting mixture was refluxed under nitrogen for 72 h and then allowed to cool to room temperature. To the cooled reaction mixture was added a solution of ferric chloride hexahydrate (52 g, excess) in acetone (200 mL), and the resulting mixture was stirred at room temperature for 1 week to decompose any unreacted iron pentacarbonyl and Fe(0) complexes that might be present. The reaction mixture was then diluted with water (300 mL) and extracted several times with ethyl acetate (7 × 100-mL portions). The combined extracts were washed with water, dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo to afford a viscous, dark brown oil. The oil was diluted with an equal volume of absolute ethanol, and the resulting solution was placed in a refrigerator and allowed to stand overnight. Under these conditions, relatively pure 3 crystallized and could be isolated simply by suction filtration (3 g, 15%). An analytical sample of 3 was obtained via column chromatography on Florisil (100–200 mesh, 10% ethyl acetate–hexane eluent); recrystallization from ethyl acetate–hexane mixed solvent afforded a colorless microcrystalline solid: mp 192.5–193.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.6–2.8 (m, 8 H), 3.0 (m, 4 H), 5.58 (m, 2 H), 7.5 (m, 6 H), 8.05 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 48.62 (d), 49.21 (d), 51.05 (d), 51.30 (d), 51.88 (d), 53.36 (d), 87.91 (d), 128.25 (d), 129.47 (d), 130.57 (s), 132.75 (d), 166.08 (s); IR (KBr) 1737 (s), 1660 (w), 1560 (w), 1520 (w), 1464 (w), 1300 (s), 1242 (s), 1200 (w), 1180 (w), 1130 (m), 1090 (w), 1072 (m), 1040 (w), 995 (w), 865 (w), 785 (m), 665 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 424 (M$^+$, 32.9), 406 (8.5), 319 (10.8), 302 (9.8), 180 (28.9), 105 (100), 77 (27.1).

Anal. Calcd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70. Found: C, 79.25; H, 5.87.

Reaction of 8 with Iron Pentacarbonyl. The same procedure described above for the reaction of 7 with iron pentacarbonyl when applied to the corresponding reaction of 8 afforded cage diester 4 in 14% yield. An analytical sample of 4 was obtained via chromatography on Florisil (100–200 mesh, 6–8% ethyl acetate–hexane eluent) followed by recrystallization from ethyl acetate–hexane mixed solvent; a colorless microcrystalline solid was thereby obtained: mp 140–141 °C; ^{1}H NMR ($CDCl_3$) δ 2.7 (m, 8 H), 2.9 (m, 4 H), 3.86 (s, 6 H), 5.5 (m, 2 H), 6.9 (upfield half of AA′BB′ pattern, 4 H), 8.0 (lowfield half of AA′BB′ pattern (4 H); ^{13}C NMR ($CDCl_3$) δ 48.75 (d), 49.34 (d), 51.24 (d), 51.45 (d), 52.05 (d), 53.54 (d), 55.37 (q), 87.78 (d), 113.61 (d), 123.21 (s), 131.59 (d), 163.41 (s), 166.00 (s); IR (KBr) 1730 (s), 1637 (s), 1535 (w), 1485 (w), 1342 (s), 1310 (s), 1290 (s), 1190 (s), 1140 (m), 1122 (m), 1100 (m), 1050 (m), 1025 (w), 967 (w), 865 (s), 783 (w) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 484 (M$^+$, 28.9), 349 (21.7), 180 (7.9), 136 (10.0), 135 (100.0), 107 (6.6), 77 (7.8). Anal. Calcd for $C_{30}H_{28}O_6$: C, 74.36; H, 5.82. Found: C, 74.50; H, 5.71.

Hydrolysis of 4. A mixture of cage diester 4 (0.80 g, 1.7 mmol), potassium hydroxide (finely ground, 0.20 g, 3.6 mmol), and water (0.2 mL) was dissolved in absolute ethanol (40 mL) and then refluxed for 3.5 h. The resulting mixture was cooled and suction-filtered. Chloroform (150 mL) was added to the filtrate, and the resulting mixture was extracted with dilute aqueous sodium bicarbonate solution. The organic layer was washed with water, dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The waxy residue thereby obtained was recrystallized from chloroform, affording cage diol 5 as a colorless microcrystalline solid (0.31 g, 85%), mp 207–209 °C. An analytical sample, mp 209.5 °C, was obtained by chromatography on Florisil (chloroform eluent) followed by recrystallization from chloroform; ^{1}H NMR (pyridine-d_5) δ 2.4–2.5 (m, 6 H), 2.64 (m, 2 H), 3.17 (m, 4 H), 4.80 (t, *J* = 1.8 Hz, 2 H), 5.4 (br s, 2 H); ^{13}C NMR (pyridine-d_5) δ 49.51 (d), 50.15 (d), 51.70 (d), 52.32 (d), 54.51 (d), 57.07 (d), 85.85 (d); IR (KBr) 3283 (vs), 2950 (s), 2875 (s), 1430 (w), 1342 (s), 1315 (m), 1309 (m), 1290 (m), 1250 (m), 1228 (s), 1197 (m), 1174 (w), 1122 (m), 1072 (s), 1040 (s), 990 (w), 915 (w), 872 (w), 804 (m), 777 (w), 672 (w) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 217 (14.5), 216 (M$^+$, 100.0), 215 (16.6), 198 (29.1), 187 (42.5), 169 (11.0), 159.1 (12.9), 141 (10.1), 129 (11.6), 128 (10.4), 115 (13.3), 107 (13.6), 105 (13.1), 104 (13.9), 103 (13.1), 91 (33.8), 79 (26.7), 78 (11.1), 77 (25.0).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.98; H, 7.61.

Oxidation of 5. Cage diol 5 (0.2 g, 0.9 mmol) was dissolved in a minimum volume of dimethyl sulfoxide; methylene chloride (3 mL) was then added. The resulting mixture was added rapidly at room temperature to a vigorously stirred mixture of pyridinium chlorochromate (PCC, 0.7, g, 3.3 mmol) in methylene chloride (4 mL). Upon addition of 5, the light orange suspension of PCC rapidly darkened. The mixture was stirred at room temperature overnight, at which time the mixture was extracted several times with ether. The combined ethereal extracts were washed with water, dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The solid residue was recrystallized from chloroform–hexane mixed solvent, affording cage diketone 6 (0.185 g, 93%) as a colorless microcrystalline solid, mp 309–311 °C (sealed tube). An analytical sample of 6, mp 313 °C, was obtained by careful column chromatography on Florisil (60–100 mesh, 1:1 chloroform–hexane eluent) followed by repeated recrystallization of the eluate from chloroform–hexane mixed solvent: ^{1}H NMR ($CDCl_3$) δ 2.4 (br, 4 H), 2.9 (br, 8 H); ^{13}C NMR ($CDCl_3$) δ 48.9 (d), 49.5 (d), 214.6 (s); IR (CCl_4 solution) 3018 (w), 2978 (m), 1787 (sh, m), 1775 (s), 1696 (s), 1321 (w), 1172 (w), 1145 (m), 892 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 212 (M$^+$, 64.1), 156 (10.7), 155 (12.1), 141 (15.0), 115 (22.4), 106 (100.0), 91 (53.3), 78 (51.1), 77 (21.0), 76 (10.1), 65 (11.7).

Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.31; H, 5.52.

Acknowledgment. Financial support of our study by the Naval Air Systems Command, The Air Force Office of Scientific Research Air Force Systems Command, Grant No. AFOSR-84-0085, The Robert A. Welch Foundation (Grant B-963), and The North Texas State University Faculty Research Committee is gratefully acknowledged.

Registry No. 3, 89278-39-7; 4, 89321-10-8; 5, 89302-19-2; 6, 89302-20-5; 7, 4796-68-3; 8, 7109-81-1; *p*-anisoyl chloride, 100-07-2; 7-norbornadienol, 822-80-0.

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