Cl)$(CH_2)_5CH_3$, 89231-77-6; $CH_2{=}CH_2$, 74-85-1; $(CH_3CH_2)_3B$, 97-94-9; $CH_3OCO(CH_2)_8CH{=}CH_2$, 111-81-9; $(CH_3OCO(CH_2)_{10})_3B$, 63399-92-8; $CH_3CH_2NH(CH_2)_7CH_3$, 4088-36-2; $CH_3OCO(CH_2)_{10}NH(CH_2)_7CH_3$·HCl, 89231-71-0; $CH_3CH_2N(SO_2C_6H_5)CHCH_3(CH_2)_5CH_3$, 89231-73-2; $CH_3OCO(CH_2)_{10}NHCHCH_3(CH_2)_5CH_3$·HCl, 89231-74-3; safrole, 94-59-7; tri[3-[3,4-(methylenedioxy)phenyl]propyl]borane, 78498-54-1; cyclohexene, 110-83-8; tricyclohexylborane, 1088-01-3; 1-(1-octylamino)-3-[3,4-(methylenedioxy)phenyl]propane hydrochloride, 89231-72-1; (1-octylamino)cyclohexane hydrochloride, 4922-19-4; 1-(2-octylamino)-3-[3,4-(methylenedioxy)phenyl]propane hydrochloride, 89231-75-4.

Synthesis of the Simple Flavonoid Broussonin A

Robert C. Ronald and Carl J. Wheeler*

Department of Chemistry, Washington State University, Pullman, Washington 99164

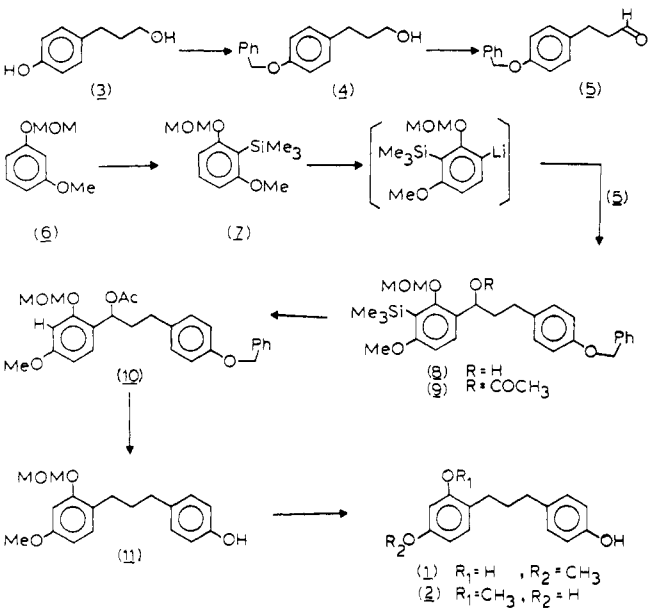
Received August 9, 1983

In 1980, Takasugi and co-workers reported the isolation and activities of several antifungal metabolites from the tissues of the paper mullberry (*Broussoneutra papyifera* Vent.) subsequent to infection with *Fusarium solani* f. sp. *mori*.[1] The structures of two previously unreported compounds were deduced by a combination of spectral and chemical degradation evidence and were assigned as broussonins A and B (**1** and **2**), respectively (Scheme I). The broussonins constitute a new type of phytoalexins, as they possess a 1,3-diarylpropane carbon skeleton. This structural feature also allows them to be classified as flavonoids and as such are among the simplest of that class of natural products to be found in nature.[2] Though syntheses have been reported for naturally occurring 1,3-diarylpropanoids lacking oxygenation on the propyl bridge,[2] they have not appeared in print to date. The synthesis of broussonin A (**1**) is the topic of this report.

For the synthesis of **1**, the primary consideration was the regiospecific introduction of the propyl chain with respect to the oxygenation patterns of both aryl rings. Conceptually, commercially available 3-(*p*-hydroxyphenyl)-1-propanol (**3**) provided a monooxygenated phenyl ring attached correctly to a propyl chain which contained latent electrophilic activation at the requisite position for subsequent anionic coupling. In practice, monobenzylation of **3**, followed by selective oxidation, provided aldehyde **5** as a suitable substrate for this type of reaction.

The work of Winkle[3] documented that metallation of methoxymethyl (MOM) protected phenols provide specific α lithiation with excellent regioselectivity in many cases when the α positions are nonequivalent. Unfortunately, with 3-(methoxymethoxy)anisole (**6**) only the 2-lithio species was available regioselectively, the 6-lithio derivative being formed only statistically with the 2-substituted isomer under altered conditions. It was reasonable to presume that selective protection of the 2 position would provide a substrate that would lithiate specifically at the 6-position and as such generate the desired nucleophile for coupling with **5**. In order to accomplish this, **6** was selectively metallated with *tert*-butyllithium, and the lithioarene was silylated with trimethylsilyl chloride to produce **7**.[4] Lithiation of **7** with *tert*-butyllithium apparently

Scheme I



provided the 6-lithiospecies, since treatment with aldehyde **5** provided the coupling product **8**. In addition to providing the desired carbon framework of the natural product with the correct arene oxygenation and substitution patterns, this coupling demonstrated the effective protection of a metallation active aryl C–H bond, thus allowing specific access to a less active metallation site.

To complete the systhesis, dihydrogenolysis of both the alcohol **8**, and the derived acetate **9** were attempted. Only debenzylated material was isolated, presumably due to inefficient catalyst contact caused by proximal steric congestion.[5] In order to circumvent this problem, mild protodesilylation of **9** provided **10**, which underwent the desired dihydrogenolysis to give **11**. Standard acidic removal of the MOM group[6] produced the synthetic natural product. Though this material would not crystallize in our hands, (lit.[1] mp 101–101.5 °C), spectral and chromatographic data have established its identity with the reported natural product,[7] thereby confirming its proposed structure and providing a viable route for its synthesis.

Experimental Section

Melting point determinations were made in open capillaries with a Thomas-Hoover Unimelt apparatus and are uncorrected. Boiling points were determined at atmospheric pressure unless noted otherwise and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian Associates EM-360 or Nicolet Technologies Corp. NT-200 spectrophotometer using tetramethylsilane as an internal standard and are reported as δ values in parts per million relative to tetramethylsilane, which equals 0. Infrared (IR) spectra were recorded on a Beckman Acculab 1 spectrophotometer and are reported in reciprocal centimeters. Gas chromatography (GLC) was performed with

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(2) Gottlieb, O. R. *Isr. J. Chem.* **1977**, *16*, 45–51, and references therein.
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(4) The rate of this reaction is noteworthy in that some 20 h are required for the reaction to reach stasis as opposed to the short (less than 1 h) reaction times usually encountered in reactions of aryllithiums. See ref 3, and references therein for typical short reactions.
(5) This hypothesis was supported by the subsequent reactions of the protodesilylated material and is consistent with the diasteromeric signals of the MOM methylene protons by ^{1}H NMR at 60 or 200 MHz in **8** and **9** but not in **10**. This observation indicates a relatively close juxtaposition of the MOM group and the optical center in the two former unreactive compounds but not in the latter reactive substrate.
(6) Yardley, J. P.; Fletcher III, H. *Synthesis* **1976**, 244.
(7) The direct comparison of synthetic and naturally occuring broussonin A by 200-MHz ^{1}H NMR, IR, and TLC employing a variety of solvent systems showed identical chemical shifts and integrated intensities, absorbances, and R_f values, respectively.

0022-3263/84/1949-1658$01.50/0

a Packard Model 417 flame-ionization gas chromatograph using a 25-m glass capillary column coated with SE-30, employing helium as the carrier gas. Preparative thin-layer chromatography was performed on 20 × 20 mm glass plates coated with a 1.5-mm layer of Merck silica gel PF-254. Column chromatography was performed in glass columns packed with J. T. Baker 60–200 mesh silica gel. All elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Reagents were used as received from commercial sources unless indicated otherwise. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Dichloromethane and hexane were purified by passage through Woelm activity I alumina and stored under nitrogen over 4Å molecular sieves. Trimethylsilyl chloride was distilled from quinoline under nitrogen prior to use. Nitrogen was purified by sequential passage through concentrated sulfuric acid, flake sodium hydroxide, and indicating calcium sulfate. Dimethylformamide (DMF) was distilled from barium oxide under nitrogen.

3-[4-(Benzyloxy)phenyl]-1-propanol (4). To a stirred suspension of sodium hydride (2.74 g, 57% by weight, 65 mmol) in DMF (60 cm^3) at room temperature was added a solution of 3-(*p*-hydroxyphenyl)-1-propanol (**3**; 9.89 g, 65 mmol) in DMF (55 cm^3) dropwise over 30 min. The solution was stirred until gas evolution ceased and then heated to 50 °C; after 20 min, benzyl chloride (8.23 g, 65 mmol) was added all at once. The reaction mixture was stirred overnight at the same temperature, cooled, poured into 700 cm^3 of water, and extracted with 400 cm^3 of ether in three portions. The combined organic phases were washed with 700 cm^3 of 3 N sodium hydroxide in two portions and 250 cm^3 of brine, dried over magnesium sulfate, and then filtered, and the filtrate was evaporated to give crude crystalline material. Recrystallization from ether/petroleum ether provided analytically pure product (12.9 g, 82%): mp 64–65 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 7.4 (s, 5 H), 7.05 (AB, 4 H, J = 9 Hz), 5.1 (s, 2 H), 3.6 (t, 2 H, J = 7 Hz), 2.5 (m, 3 H), 1.8 (m, 2 H); IR (neat) 3620, 3450, 2940, 1505, 1250 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.45; H, 7.69.

3-[4-(Benzyloxy)phenyl]-1-propanal (5). To a stirred suspension of pyridinium dichromate (7.64 g, 20 mmol) in methylene chloride (60 cm^3) at room temperature was added compound **4** (2.43 g, 10 mmol) all at once as a solid. The reaction vessel was flushed with nitrogen, stoppered, and stirred for 22 h. The volume was then reduced in vacuo by approximately 35 cm^3, 70 cm^3 of ether was added, the slurry was filtered through Celite, and the residue was rinsed with ether to produce a final filtrate volume of 250 cm^3. The filtrate was washed sequentially with 500 cm^3 of dilute cupric sulfate in three portions, 125 cm^3 of saturated sodium bicarbonate, 125 cm^3 of brine, then dried over magnesium sulfate, and then filtered, and the filtrate was evaporated in vacuo to give a light brown oil, which solidified on standing. Filtration through silica gel with dichloromethane provided a colorless oil (1.91 g, 79%), which solidified to a waxy solid: mp 41–42 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 9.85 (d, 1 H, J = 1 Hz), 7.4 (s, 5 H), 7.1 (AB, 4 H, J = 9 Hz), 5.0 (s, 2 H), 2.75 (m, 4 H); IR (neat) 3140, 2830, 2740, 1720, 1510, 1240 cm^{-1}. Anal. Calcd, as the 2,4-dinitrophenylhydrazone (mp 150–151 °C), for $C_{22}H_{20}O_5N_4$: C, 62.85; H, 4.80. Found: C, 63.00; H, 4.92.

3-Methoxy-2-(trimethylsilyl)-1-(methoxymethoxy)benzene (7). To a stirred solution of 3-methoxymethoxy anisole (**6**; 4.01 g, 24 mmol) in hexane (60 cm^3) at 0 °C was added *tert*-butyllithium in pentane (15.4 cm^3, 1.6 M) dropwise over 15 min. After the solution was stirred for an additional 2 h at 0 °C, cold THF (20 cm^3) was added in a slow stream to dissolve the precipitate, followed by the addition of neat trimethylsilyl chloride (3.25 g, 30 mmol). The cold bath was removed, and the mixture was allowed to warm with stirring to room temperature. After 20 h the slurry was poured into 100 cm^3 of 14% aqueous ammonium chloride and extracted with 140 cm^3 of ether in two portions. The combined organic phases were washed with brine, dried over magnesium sulfate, and then filtered, and the filtrate was evaporated in vacuo to provide crude product. Fractional distillation (97–99 °C, 0.48–0.50 torr) provided **7** (4.08 g, 72%) in greater than 97% purity as assessed by GLC. Preparative TLC (10% ether/hexane), followed by evaporative distillation, provided analytical material: ^1H NMR (200 MHz, $CDCl_3$) δ 7.23 (t, 1 H, J = 8.25 Hz), 6.69 (dd, 1 H, J_1 = 0.64 Hz, J_2 = 8.25 Hz), 6.50 (dd, 1 H, J_1 = 0.61 Hz, J_2 = 8.25 Hz), 5.12 (s, 2 H), 3.73 (s, 3 H), 3.45 (s, 3 H), 0.31 (s, 9 Hz); IR (neat) 2975, 1580, 1455, 1235, 1070, 880 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3Si$: C, 59.96; H, 8.39. Found: C, 59.76; H, 8.59.

1-[4-Methoxy-2-(methoxymethoxy)-3-(trimethylsilyl)-phenyl]-3-[4-(benzyloxy)phenyl]-1-propanol (8). To a magnetically stirred solution of **7** (1.13 g, 4.7 mmol) in hexane (24 cm^3) at 0 °C was added a solution of *tert*-butyllithium in pentane (3.09 cm^3, 1.6 M) in a slow stream. After 4.5 h, THF (12 cm^3) was added dropwise over 15 min, followed in 10 min by the slow dropwise addition of **5** (1.14 g, 4.75 mmol) in THF (24 cm^3) over 30 min. During the addition all the precipitate dissolved. The solution was stirred for an additional 2 h at 0–10 °C and then poured into 200 cm^3 of 14% aqueous ammonium chloride, and extracted with 250 cm^3 of ether in two portions. The combined organic phases were washed with 100 cm^3 of brine, dried over magnesium sulfate, and then filtered, and the filtrate was evaporated in vacuo to afford crude product. Column chromatography (2:48:50 methanol/dichloromethane/hexane) provided starting arylsilane **7** (0.190 g, 17% recovery) and the desired product **8** (1.62 g, 72% isolated, 86% based on consumed silane). Preparative TLC (2:1 ether/hexane), followed by evaporative distillation, provided analytical material: ^1H NMR (200 MHz, $CDCl_3$) δ 7.47–7.27 (m, 6 H), 7.12 (AB, 2 H, J = 8.68 Hz), 6.87 (AB, 2 H, J = 8.68 Hz), 6.52 (d, 1 H, J = 8.56 Hz), 5.00 (s, 2 H), 4.99–4.87 (m, 2 H, includes AB at δ 4.91 with J = 6.01 Hz), 4.78 (AB, 1 H, J = 6.01 Hz), 3.74 (s, 3 H), 3.40 (s, 3 H), 3.14 (m, 1 H), 2.95–2.50 (m, 2 H), 2.40–1.65 (m, 2 H), 0.30 (s, 9 H); IR (neat) 3450, 1510, 1240, 1060, 840 cm^{-1}. Anal. Calcd for $C_{28}H_{36}O_5Si$: C, 69.97; H, 7.55. Found: C, 70.24; H, 7.71.

1-[4-Methoxy-2-(methoxymethoxy)-3-(trimethylsilyl)-phenyl]-3-[4-(benzyloxy)phenyl]-1-propyl Acetate (9). To a solution of alcohol **10** (1.616 g, 3.36 mmol) in pyridine (25 cm^3) was added acetic anhydride (7 cm^3) with stirring. The solution was heated to 100–110 °C for 30 min, cooled to room temperature, poured into 500 cm^3 of ice-cold 1 N HCl, and extracted with 300 cm^3 of ether in three portions. The combined organic phases were washed with 100 cm^3 saturated sodium bicarbonate, dried over magnesium sulfate, and then filtered, and the filtrate was evaporated in vacuo to afford crude product. Filtration through silica with 2:1 hexane/ether, removal of solvent, and prolonged vacuum dessication provided pure product (1.621 g, 92%): ^1H NMR (200 MHz, $CDCl_3$) δ 7.43–7.28 (m, 6 H), 7.08 (AB, 2 H, J = 8.68 Hz), 6.87 (AB, 2 H, J = 8.68 Hz), 6.64 (d, 1 H, J = 8.58 Hz), 6.17 (dd, 1 H, J_1 = 5.53 Hz, J_2 = 7.94 Hz), 5.00 (2, 2 H), 4.97 (AB, 1 H, J = 5.17 Hz), 4.87 (AB, 1 H, J = 5.18 Hz), 3.74 (s, 3 H), 3.45 (s, 3 H), 2.69–2.48 (m, 2 H), 2.28–1.91 (m, 5 H, includes singlet at δ 2.05), 0.31 (s, 9 H); IR (neat) 3050, 2955, 1735, 1585, 1510, 1245, 730 cm^{-1}. Anal. Calcd for $C_{30}H_{38}O_6Si$: C, 68.93; H, 7.33. Found: C, 68.70; H, 7.43.

1-[4-Methoxy-2-(methoxymethoxy)phenyl]-3-[4-(benzyloxy)phenyl]-1-propyl Acetate (10). To neat **9** (1.189 g, 2.27 mmol) with stirring was added a solution of tetraethylammonium fluoride in THF (10 cm^3, 1 M). The reaction vessel was purged with nitrogen, stoppered, and stirred for 24 h at room temperature. The deep burgundy solution was poured into 100 cm^3 of 14% aqueous ammonium chloride and extracted with 100 cm^3 of ether in two portions. The combined organic phases were washed with 50 cm^3 of saturated sodium bicarbonate and then 50 cm^3 of brine, dried over magnesium sulfate, and then filtered, and the filtrate was evaporated in vacuo to afford crude product. Column chromatography (1:1 ether/hexane) provided pure product (0.893 g, 87%): ^1H NMR (200 MHz, $CDCl_3$) δ 7.47–7.20 (m, 6 H, includes doublet at δ 7.24 with J = 8.52 Hz), 7.07 (AB, 2 H, J = 8.72 Hz), 6.87 (AB, 2 Hz, J = 8.73 Hz), 6.67 (d, 1 H, J = 2.42 Hz), 6.54 (dd, 1 H, J_1 = 2.44 Hz, J_2 = 8.52 Hz), 6.14 (dd, 1 H, J_1 = 7.25 Hz, J_2 = 5.97 Hz), 5.15 (s, 2 H), 5.02 (s, 2 H), 3.77 (s, 3 H), 3.44 (s, 3 H), 2.64–2.44 (m, 2 H), 2.18–2.01 (m, 5 H, includes singlet at δ 2.05); IR (neat) 3040, 2970, 1735, 1615, 1510, 1240 cm^{-1}. Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.89; H, 6.80.

4-[3-[4-Methoxy-2-(methoxymethoxy)phenyl]propyl]-phenol (11). To a stirred solution of acetate **10** (0.163 g, 0.362 mmol) in ethyl acetate (3 cm^3) and ethanol (1 cm^3) was added 10% palladium on carbon catalyst (Research Organic/Inorganic Chemical Co., 0.050 g). The solution was evacuated by aspiration, and hydrogen was introduced. This cycle was repeated four times,

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: ^1H 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%); ^1H 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); ^1H 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

Alan P. Marchand*

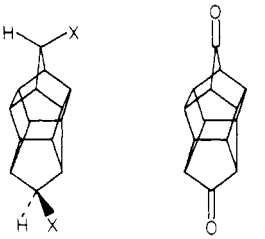
Department of Chemistry, North Texas State University, NTSU Station, Denton, Texas 76203

Arthur D. Earlywine

Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73019

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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