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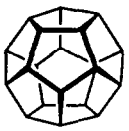
DEVELOPMENT OF A STRATEGY FOR THE SYNTHESIS OF THE SPHERICAL HYDROCARBON *p*-[$4^2.5^8$]DECAHEDRANE

Chien-Chang Shen and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Abstract: A directed synthesis of triketone **20**, an immediate precursor to a "capped" [4]peristylane, has been accomplished in 10 laboratory operations. Starting from the previously described cyclobutanone **11**, a fulvene is formed and transformed into **13** by means of a Diels-Alder cycloaddition. The C_s symmetry of this early intermediate is preserved throughout the remainder of the scheme. Once a cyclopentadiene ring is annealed as in **14**, the cyclobutane base is elaborated by [4+2]π addition of (*Z*)-1,2-bis(phenylsulfonyl)ethylene from below-plane, reductive desulfonylation, and [2+2] photocyclization. Following cleavage of the oxirane ring with periodic acid, arrival at **20** required debenzylation and oxidation. Unfortunately, the efficiency of this pathway is low (0.05% overall) and requires optimization before subsequent transformations that could produce **2** can be implemented.

An insightful analysis by Garratt and White of the topology of saturated $(CH)_{2n}$ hydrocarbons appeared in 1977.[1] They recognized that systems having an odd value of *n* would likely have properties quite distinctive from those in which *n* is even. Furthermore, the latter class was demonstrated to encompass a series of highly symmetric molecules which feature a central ring of *n* methine units linked to a pair of *n*/2-membered rings by alternate carbon atoms. When *n* = 10, the compound is recognized to be dodecahedrane (**1**), the synthesis[2] and X-ray crystallographic analysis[3] of which



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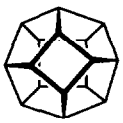
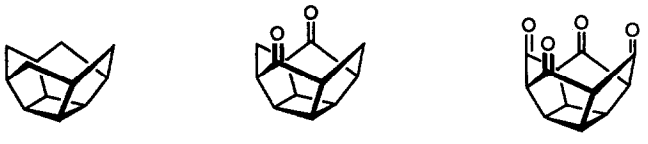


2

3

were announced some time ago.[4] de Meijere and co-workers recently described the synthesis and solid-state structure of *p*-[$3^2.5^6$]octahedrane (**3**),[5] the smallest member of this subset.[6] These developments prompt us to report the results of a preliminary investigation designed to gain access ultimately to **2**, the title compound which is presently unknown.

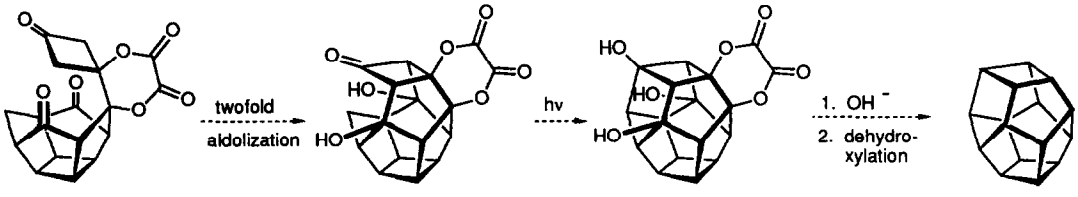
A key substructural component of **2** is the [4]peristylane framework (**4**), an expedient route to which has been developed in these laboratories.[6,7] Subsequently, means for the introduction of carbonyl groups along the fluted perimeter of **4** as in the 2,6-dione **5**,[8] the 2,4,6-trione,[9] and tetraketone **6**[10] were uncovered. Since the regiochemical and topological aspects of the processes leading to these molecules had been brought under control,[7-11] extensions to the preparation of **2**



4 5 6

were considered possible if a suitable means for "capping" the peristylane foundation could be devised.

Historically, approaches to spherical molecules by one or another "capping" protocol have been uniformly unsuccessful. The more well known of these are the recalcitrant triquinacene dimerization problem,[12] the inability to cyclize *dl*-bivalvane,[13] and the failure to roof [5]peristylane.[14] Notwithstanding, a logical outgrowth of our past accomplishments was the rational design of triketone **7** for use in a twofold aldol condensation. With the availability of **8**, a homo-Norrish photocyclization[2,15] might be feasible either prior to or following removal of the oxygen-containing substituents. Described herein is a workable synthetic pathway to an immediate precursor of **7**.



7 8 9 2

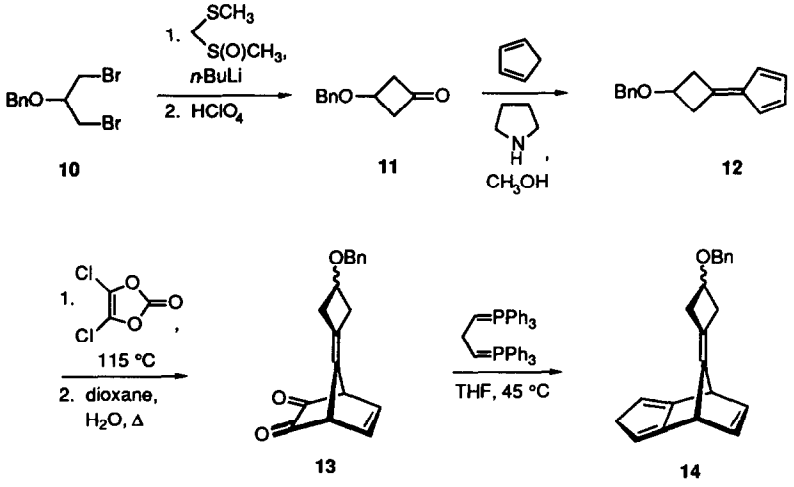
Results and Discussion

With the adoption of this retrosynthetic analysis, the initial preparative goal became the functionalized isodicyclopentatriene **14**. To this end, benzyl bromide and epibromohydrin were admixed in the presence of a catalytic quantity of mercuric chloride to generate **10**[16] (Scheme I). Base-promoted condensation of this dibromide with methyl methylthiomethyl sulfoxide and subsequent hydrolysis as described by Tsuchihashi[17] furnished cyclobutanone **11**. When this ketone was treated with freshly distilled cyclopentadiene and pyrrolidine in methanol at room temperature,[18] fulvene **12** was obtained in 55% yield as a yellow oil.

With **12** conveniently available, its Diels-Alder cycloaddition with dichlorovinylene carbonate[19] was accomplished by heating in the absence of solvent at 115 °C for 1 h under nitrogen. Direct hydrolysis led to the isolation of **13** in rather low yield (26%). Various attempts to improve the efficiency of this reaction were to no avail. NMR analysis indicated that the two diastereomers were present in a ratio of approximately 5:4. A double Wittig reaction involving **13** and the bisphosphonium salt derived from 1,3-dibromopropane[20] gave **14** whose structural constitution was fully consistent with its spectroscopic properties.

As in the case of the parent tricyclo[5.2.1.$0^{2,6}$]deca-2,5,8-triene,[21] **14** exhibits a kinetic preference for below-plane dienophile capture. With (*Z*)-1,2-bis(phenylsulfonyl)ethylene,[22] [4+2]

Scheme I



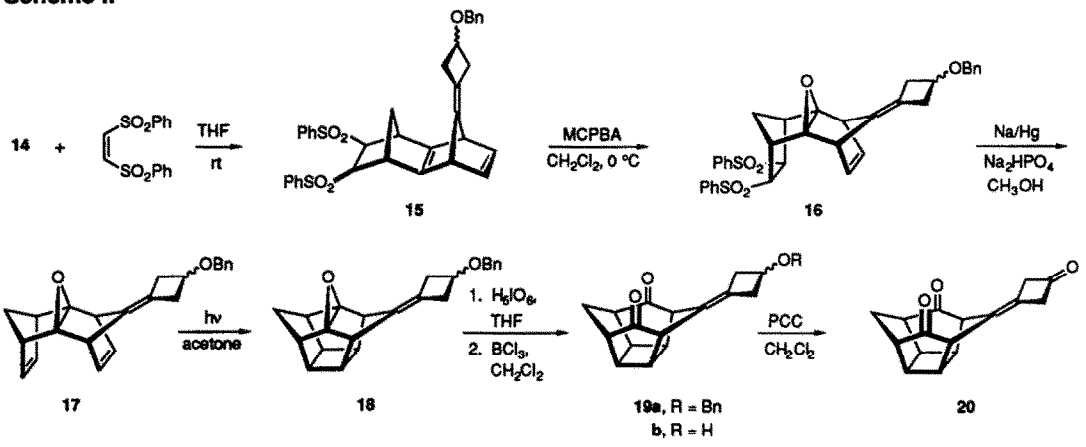
cycloaddition occurred to precipitate **15** from solution (Scheme II). Characterization of **15** as the *syn*-sesquinorbornadiene stereoisomer was realized by peracid oxidation to give epoxide **16**. In line with past observations,[8a,23] apical protons syn to the oxirane ring are shielded as a consequence of their proximity to the oxygen atom. In addition, reductive desulfonylation of **16** with 1.5% sodium amalgam in buffered methanol[8a,24] generated a second norbornenyl double bond which resides in close spatial proximity to the one originally present. As a consequence, sensitized irradiation of acetone solutions of **17** in a Rayonet reactor with a bank of 350 nm lamps promoted facile [2+2] cycloaddition and formation of cage compound **18**.

The success of the photochemical ring closure just described sets the stage for subsequent cleavage of the epoxide ring with periodic acid in tetrahydrofuran.[25] This oxidation produced diketone **19a** in which a properly functionalized [4]peristylane substructure has been fully elaborated.

For reasons unknown to us, attempts to remove the benzyl blocking group in **19a** via hydrogenolysis proved problematical. Nor did recourse to trimethylsilyl iodide liberate the hydroxyl substituent. The conversion to **19b** was ultimately realized by reaction with boron trichloride in CH_2Cl_2.[26] PCC oxidation of this intermediate to provide triketone **20** proved uneventful.

With arrival at **20**, the synthesis of a possible precursor to **2** has been realized in 10 laboratory operations. While the synthetic route offers several expedient bond-forming strategies and benefits from the involvement of symmetric intermediates, it is quite inefficient at several points and is chromatography intensive. Thus, the overall yield from **11** is only 0.05%. Any further utilization of this scheme as a means for approaching **2** demands that improvement be brought to such individual steps as the Diels-Alder cycloaddition leading to **13** and the cyclopentadiene ring annulation that delivers **14**. Other conditions also need to be developed for crafting the cyclobutane base in **18** via generation of **17** and its excited-state ring closure. Optimization along these lines will make far less arduous the acquisition of **20** in quantities necessary to develop workable protocols that could ultimately lead to reasonable amounts of p-[$4^2.5^8$]decahedrane.

Scheme II



Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1320 spectrometer. ^1H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz on Bruker instruments. Mass spectra were recorded on a Kratos MS-30 instrument at The Ohio State University Campus Chemical Instrument Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark. The organic extracts were dried over anhydrous magnesium or sodium sulfate. Solvents were reagent grade and in many cases dried prior to use.

Benzyl 3-(2,4-cyclopentadien-1-ylidene)cyclobutyl Ether(12). To a solution of cyclopentadiene (18.4 g, 0.278 mol) and **11** (19.5 g, 0.111 mol) in methanol (110 mL) was added 11.9 g (0.167 mol) of pyrrolidine under an atmosphere of argon. The resultant brown solution was stirred at rt for 6 h, at which point glacial acetic acid (10.7 g) was introduced. The product was taken up in ether and washed with water and brine. The organic phase was dried and evaporated to leave a residue which was purified by chromatography (silica gel, elution with 3:1 petroleum ether-CH_2Cl_2). There was obtained 13.6 g (55%) of **12** as a yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47-7.25 (m, 5 H), 6.43 (d, J = 5.1 Hz, 2 H), 6.26-6.24 (m, 2 H), 4.48 (s, 2 H), 4.23 (quint, J = 6.3 Hz, 1 H), 3.37-3.28 (m, 2 H), 3.13-3.04 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 149.4, 140.1, 137.7, 130.8, 128.4, 127.8, 127.7, 120.3, 70.7, 68.7, 40.6; MS *m/z* (M^+) calcd 224.1201, obsd 224.1269.

7-[3-(Benzyloxy)cyclobutylidene]bicyclo[2.2.1]hept-5-ene-2,3-dione (13). A magnetically stirred mixture of **12** (1.78 g, 7.94 mmol) and dichlorovinylene carbonate (5.09 g, 32.9 mmol) was heated at 115 °C under N_2 for 1 h. The cooled reaction mixture was taken up in dioxane (25 mL) and water (15 mL) and heated at reflux for 3 h. After several extractions with CH_2Cl_2, the combined organic extracts were washed with water and brine, dried, and concentrated. Chromatography of the residue (silica gel, elution with 3:1 petroleum ether-ethyl acetate) gave 589 mg (26%) of **13** as an orange solid, mp 79-82 °C, composed of a 5:4 mixture of diastereomers; IR (KBr, cm^{-1}) 1760, 1550,

1495, 1460, 1345, 1120, 1090, 1000; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.25 (m, 5 H), 6.57-6.52 (m, 2 H), 4.44 (s, 2 H), 4.21-4.09 (m, 1 H), 3.66-3.62 (m, 2 H), 3.01-2.91 (m, 2 H), 2.82-2.65 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) ppm 191.3, 137.6, 137.4, 133.5, 128.9, 128.3, 127.74, 127.70, 70.6, 68.7, 55.6, 38.4; (minor isomer) characteristic peaks at 191.1, 137.2, 128.7, 70.5, 68.8, 55.5; MS *m/z* (M^+-C_2O_2) calcd 224.1201, obsd 224.1243.

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.84; H, 5.89.

8-[3-(Benzyloxy)cyclobutylidene]-4,7-dihydro-4,7-methano-2*H*-indene (14). To a suspension of 1,3-propanebis(triphenylphosphonium)bromide (1.42 g, 1.96 mmol) in dry THF (25 mL) was added dropwise 2.6 mL of 1.5 M *n*-butyllithium under an atmosphere of argon at rt. After 10.5 h, a solution of **13** (547 mg, 1.95 mmol) in THF (20 mL) was introduced dropwise. The mixture was stirred for 2 h, heated at 45 °C for 2 days, and quenched with water. The product was extracted into pentane and this solution was washed with water and brine prior to drying and evaporation. The residue was purified by silica gel chromatography (elution with 20:1 petroleum ether-ethyl acetate) to give **14** (103 mg, 20%) as a yellowish liquid composed of two diastereomers in a 5:4 ratio; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.23 (m, 5 H), 6.48 (m, 2 H), 5.67 (m, 2 H), 4.38 (s, 2 H), 4.06 and 4.02 (two qunitets, J = 6.6 Hz, total of 1 H), 3.76 (m, 2 H), 3.23 (t, J = 1.4 Hz, 2 H), 2.86-2.76 (m, 2 H), 2.66-2.58 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 151.9, 150.5, 138.7, 138.1, 128.2, 127.7, 127.5, 114.1, 107.3, 70.2, 69.3, 46.0, 44.9, 37.1; (minor isomer) characteristic peaks at 138.6, 114.2, 45.0, 37.3.

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.18; H, 7.12.

(1*R,2*R**,3*S**,4*S**,5*R**,8*S**)-9-[3-(Benzyloxy)cyclobutylidene]-1,2,3,4,5,6-hexahydro-2,3-bis(phenylsulfonyl)-1,4:5,8-dimethanonaphthalene (15).** A solution of **14** (348 mg, 1.21 mmol) and (*Z*)-1,2-bis(phenylsulfonyl)ethylene (373 mg, 1.21 mmol) in THF (3 mL) was stirred at rt under an argon atmosphere for 2 days. The resulting white precipitate was collected by filtration, washed with hexanes, and dried to give 348 mg (48%) of **15** as a white solid, mp 164 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 7.9 Hz, 4 H), 7.67-7.52 (m, 6 H), 7.30-7.24 (m, 5 H), 6.60 (t, J = 1.7 Hz, 2 H), 4.35 (s, 2 H), 3.97 (quintet, J = 6.6 Hz, 1 H), 3.54 (br s, 2 H), 3.37 (br s, 2 H), 2.73 (d, J = 1.7 Hz, 2 H), 2.70-2.59 (m, 3 H), 2.50-2.42 (m, 2 H), 1.64 (d, J = 10 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) ppm 159.7, 157.5, 140.8, 139.2, 137.9, 133.5, 128.9, 128.3, 128.2, 127.7, 127.5, 98.9, 70.3, 69.2, 64.2, 48.8, 47.1, 43.6, 36.6; (minor isomer) characteristic peaks at 159.9, 157.6, 48.9, 36.8; FAB MS *m/z* (M^++H) calcd 597.26, obsd 597.26.

(1*R,2*R**,3*S**,4*S**,4a*R**,5*R**,8*S**,8a*S**)-10-[3-(Benzyloxy)cyclobutylidene]-1,2,3,4,5,8-hexahydro-2,3-bis(phenylsulfonyl)-4a,8a-epoxy-1,4:5,8-dimethano-naphthalene (16).** A cold (-10 °C), magnetically stirred solution of **15** (324 mg, 0.543 mmol) in CH_2Cl_2 (20 mL) was treated dropwise with a solution of *m*-chloroperbenzoic acid (118 mg) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at 0 °C for 6 h, the white precipitate was filtered off, and the filtrate was washed with 5% $NaHSO_3$ and saturated $NaHCO_3$ solutions, water, and brine prior to dryng and concentration. After crystallization from CH_2Cl_2-hexanes, **16** was obtained as colorless crystals, mp 155 °C (dec) (258 mg, 78%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 4 H), 7.68-7.50 (m, 6 H), 7.33-7.19 (m, 5 H), 6.53 (br s, 2 H), 4.38 (s, 2 H), 3.98 and 3.90 (two quintets, J = 6.6 Hz each, total 1 H), 3.71 (d, J = 2.1 Hz, 2 H), 3.19 (s, 2 H), 2.98 (br s, 2 H), 2.67-2.26 (series of m, 5 H), 1.91 (d, J = 11 Hz, 1

H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) ppm 145.8, 140.3, 140.1, 137.8, 133.7, 129.1, 128.2, 128.1, 127.6, 127.4, 106.6, 70.2, 69.2, 66.6, 64.4, 46.4, 43.7, 36.6, 34.9; (minor isomer) characteristic peaks at 106.5, 70.1, 68.8, 66.7, 64.7, 46.7, 43.8; MS *m/z* (M^+-$CH_2C_6H_5$) calcd 521.1092, obsd 521.1144.

(1*R,4*S**,4a*R**,5*S**,8*R**,8a*S**)-10-[3-(Benzyloxy)cyclobutylidene]-1,4:5,8-tetrahydro-4a,8a-epoxy-1,4:5.8-dimethanonaphthalene (17).** To a magnetically stirred mixture of **16** (499 mg, 0.814 mmol) and disodium hydrogen phosphate (830 mg) in methanol (12 mL) was added 1.5% sodium amalgam (14.4 g) in portions under argon over a period of 5 h. After an additional 3 h of stirring, water was added and the mixture was extracted with CH_2Cl_2. The combined organic phases were washed with water and brine, dried and concentrated to give 247 mg of crude **17** as a viscous brownish oil, which was irradiated without further purification; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32-7.24 (m, 5 H), 6.23 (t, *J* = 1.8 Hz, 2 H), 6.07 (br s, 2 H), 4.37 (s, 2 H), 4.08 and 3.95 (two quintets, *J* = 6.6 each, total 1 H), 3.38 (br s, 2 H), 3.03 (br s, 2 H), 2.81-2.42 (m, 4 H), 2.05 (d, *J* = 7.7 Hz, 1 H), 1.27 (d, *J* = 7.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) ppm 146.1, 143.2, 142.7, 137.8, 127.9, 127.5, 127.4, 76.4, 69.9, 69.3, 50.2, 47.6, 45.0, 36.6; (minor isomer) characteristic peaks at 128.0, 104.2, 69.8, 68.9, 47.9, 45.1, 36.5; MS *m/z* (M^+) calcd 330.1619, obsd 330.1683.

3-[3-(Benzyloxy)cyclobutylidene]octahydro-4a,6b-epoxy-1,5:2,4-ethanediylidenecyclopenta[*cd*]pentalene (18). The unpurified sample of **17** from above was dissolved in acetone (20 mL), placed in a pyrex tube, and irradiated in a Rayonet reactor with a full bank of 3500 Å lamps for 24 h. After solvent evaporation, the residue was purified by silica gel chromatography (gradient elution with 1:1 petroleum ether-CH_2Cl_2 to pure CH_2Cl_2) to furnish 61 mg (23% from **16**) of **18**. An analytical sample was obtained by preparative TLC on silica gel (elution with 15:1 petroleum ether-ethyl acetate); colorless solid, mp 131-134 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.22 (m, 5 H), 4.40 (s, 2 H), 4.11 and 4.03 (two quintets, *J* = 6.7 each, total 1 H), 2.91-1.54 (series of m, 10 H), 2.28 (s, 2 H), 1.51 (d, *J* = 10.9 Hz, 1 H), 1.26 (d, *J* = 10.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) ppm 138.1, 136.9, 128.2, 127.8, 127.5 120.6, 70.3, 69.5, 62.6, 41.1, 40.7, 39.4, 38.7, 37.8, 32.52; (minor isomer) characteristic peaks at 136.5, 127.7, 120.3, 70.1, 69.3, 62.9, 41.0, 40.6, 39.0, 37.9, 32.45; MS *m/z* (M^+-$CH_2C_6H_5$) calcd 239.1072, obsd 239.1083.

7-[3-(Benzyloxy)cyclobutylidene]octahydro-1,6:3,4-dimethanocyclobuta[1,2:3,4]dicyclopentene-2,5-dione (19a). A solution of **18** (43 mg, 0.129 mmol) and periodic acid (30 mg, 0.133 mmol) in tetrahydrofuran (10 mL) was stirred at rt for 5 h. The product was extracted into CH_2Cl_2, washed with 10% $NaHSO_3$ solution and brine, dried, and freed of solvent. Purification of the residue by preparative TLC (elution with 1:1 petroleum ether-ethyl acetate) gave 24 mg (53%) of **19a** as a colorless solid, mp 159-163.5 °C; IR (KBr, cm^{-1}) 1730, 1495, 1455, 1345, 1150, 1120, 755, 705; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45-7.24 (m, 5 H), 4.44 (s, 2 H), 4.23-4.06 (m, 1 H), 3.50 (br s, 5 H), 3.29-3.18 (m, 3 H), 2.92 (br s, 1 H), 2.72-2.64 (m, 3 H), 2.42-2.21 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) ppm 222.6, 138.0, 134.2, 131.6, 128.3, 127.8, 127.6, 70.4, 68.7, 57.0, 53.2, 43.5, 42.1, 39.9, 38.4; (minor isomer) characteristic peaks at 221.7, 133.4, 131.2, 70.2, 69.6, 57.3, 53.0, 43.7, 41.3; MS *m/z* (M^+) calcd 346.1569, obsd 346.1516.

Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.81; H, 6.44.

Octahydro-7-(3-hydroxycyclobutylidene]-1,6:3,4-dimethanocyclobuta[1,2:3,4]dicyclo-

pentene-2,5-dione (19b). To a magnetically stirred solution of **19a** (20 mg, 0.058 mmol) in CH_2Cl_2 (5 mL) was added a solution of boron trichloride in CH_2Cl_2 (0.5 mL of 1.0 M) at -78 °C. After the temperature rose gradually to 0 °C during 4.5 h, the reaction mixture was recooled to -78 °C and quenched with methanol (1 mL). When the temperature reached to 20 °C, the solution was washed with water and brine, dried, and concentrated. After preparative TLC on silica gel (elution with 1:4 petroleum ether-ethyl acetate), there was isolated 8 mg (52%) of **19b** as a white solid, mp 140-147 °C; IR (KBr, cm^{-1}) 1720, 1450, 1410, 1230, 1165, 1100, 1050, 720; ^1H NMR (300 MHz, $CDCl_3$) (major isomer) δ 4.48 (m, 1 H), 3.51 (br s, 4 H), 3.35-3.27 (m, 1 H), 3.19 (br s, 2 H), 2.64-2.55 (m, 2 H), 2.71 (m, 2 H), 2.41-2.20 (m, 2 H), 1.98 (br s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) (major isomer) ppm 222.7, 134.3, 131.2, 63.2, 57.0, 53.3, 43.6, 43.0, 42.1, 41.2; (minor isomer) characteristic peaks at 222.1, 133.5, 130.3, 64.4, 57.3, 53.1, 43.7, 41.3; MS *m/z* (M^+) calcd 256.1099, obsd 256.1137.

Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.48; H, 6.35.

Octahydro-7-(3-oxocyclobutylidene]-1,6:3,4-dimethanocyclobuta[1,2:3,4]dicyclopentene-2,5-dione (20). To a magnetically stirred solution of **19b** (11 mg, 0.043 mmol) in CH_2Cl_2 (5 mL) was added pyridinium chlorochromate (14 mg, 0.065 mmol). After being stirred at rt for 7 h, the reaction mixture was washed with water and brine, dried, and concentrated to give **20** as a white solid, mp 197-198 °C (9 mg, 79%); IR (KBr, cm^{-1}) 1800, 1720, 1705, 1375, 1225, 1165, 1150, 1115, 1050; ^1H NMR (300 MHz, $CDCl_3$) δ 3.98-3.88 (m, 2 H), 3.64-3.55 (m, 6 H), 3.29 (br s, 2 H), 2.78 (m, 2 H), 2.44-2.24 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 222.0, 204.1, 136.1, 123.3, 58.4, 54.4, 53.1, 43.7, 42.2, 41.1; MS *m/z* (M^+) calcd 254.0943, obsd 254.0953.

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.47; H, 5.55.

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References and Notes

(1) Garratt, P. J.; White, J. F. *J. Org. Chem.* **1977**, *42*, 1733.

(2) (a) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (b) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. *J. Am. Chem. Soc.* **1983**, *105*, 5446. (c) See also Fessner, W.-D.; Murty, B. A. R. C.; Wörth, J.; Hunkler, D.; Fritz, H.; Prinzbach, H.; Roth, W. D.; von R. Schleyer, P.; McEwen, A. B.; Maier, W. F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 452.

(3) Gallucci, J. C.; Doecke, C. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 1343.

(4) Reviews: (a) Paquette, L. A. In *Strategies and Tactics in Organic Synthesis*, Lindberg, T., Ed.: Academic Press, New York, 1984, pp 175 ff. (b) Paquette, L. A. *Chem. Rev.* **1989**, *89*, 1051. (c) Paquette, L. A. In *Cage Hydrocarbons*, Olah, G. A., Ed.: John Wiley and Sons, Inc., New York, 1990, pp 313 ff.

(5) Lee, C.-H.; Liang, S.; Haumann, T.; Boese, R.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 559.

(6) For an explanation of this nomenclature, consult Paquette, L., A.; Browne, A. R.; Doecke, C. W.; Williams, R. V. *J. Am. Chem. Soc.* **1983**, *105*, 4113, footnote 4.

(7) Paquette, L. A.; Fischer, J. W.; Browne, A. R.; Doecke, C. W. *J. Am. Chem. Soc.* **1985**,

107, 686.

(8) (a) Paquette, L. A.; Künzer, H.; Green, K. E.; De Lucchi, O.; Licini, G.; Pasquato, L.; Valle, G. *J. Am. Chem. Soc.* **1986**, *108*, 3453. (b) Engel, P.; Fischer, J. W.; Paquette, L. A. *Z. Kristallogr.* **1984**, *166*, 225.

(9) Paquette, L. A.; Shen, C.-C. *Tetrahedron Lett.* **1988**, *29*, 4069.

(10) Paquette, L. A.; Shen, C.-C.; Engel, P. *J. Org. Chem.* **1989**, *54*, 3329.

(11) (a) Paquette, L. A.; Fischer, J. W.; Engel, P. *J. Org. Chem.* **1985**, *50*, 2524. (b) Waykole, L. M.; Shen, C.-C.; Paquette, L. A. *J. Org. Chem.* **1988**, *53*, 4969. (c) Shen, C.-C.; Paquette, L. A. *J. Org. Chem.* **1989**, *54*, 3324.

(12) (a) Woodward, R. B.; Fukunaga, T.; Kelly, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 3162. (b) Jacobson, I. T. *Acta Chem. Scand.* **1967**, *21*, 2235. (c) Paquette, L. A.; Farnham, W. B.; Ley, S. V. *J. Am. Chem. Soc.* **1974**, *96*, 312. (d) Repic, O. Ph.D. Dissertation, Harvard University, 1976. (e) Paquette, L. A.; Itoh, I.; Lipkowitz, K. B. *J. Org. Chem.* **1976**, *41*, 3524. (f) Deslongchamps, P.; Soucy, P. *Tetrahedron* **1981**, *37*, 4385. (g) Roberts, W. P.; Shoham, G. *Tetrahedron Lett.* **1981**, *22*, 4895. (h) Roberts W. P. Ph.D. Dissertation, Harvard University, 1982. (i) Almansa, C.; Moyano, A.; Serratosa, F. *Tetrahedron* **1988**, *44*, 2657. (j) Bertz, S. H.; Kourouklis, G. A.; Jayaraman, A.; Lannoye, G.; Cook, J. M. *Can. J. Chem.* **1993**, *71*, 352.

(13) (a) Paquette, L. A.; Itoh, I.; Farnham, W. B. *J. Am. Chem. Soc.* **1975**, *97*, 7280. (b) Clardy, J.; Solheim, B. A.; Springer, J. P.; Itoh, I.; Paquette, L. A. *J. Chem. Soc. Perkin Trans. 2* **1979**, 296.

(14) Eaton, P. E.; Bunnelle, W. H.; Engel, P. *Can. J. Chem.* **1984**, *62*, 2612.

(15) (a) Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. G. *Science* **1981**, *211*, 575. (b) Paquette, L. A.; Balogh, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 774. (c) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Taylor, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 5441. (d) Paquette, L. A.; Miyahara, Y. *J. Org. Chem.* **1987**, *52*, 1265.

(16) Avram, M.; Nenitzescu, C. D.; Maxim, M. *Chem. Ber.* **1957**, *90*, 1424.

(17) Ogura, K.; Yamashita, M.; Suzuki, M.; Furukawa, S.; Tsuchihashi, G. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1637.

(18) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.

(19) (a) Scharf, H. D.; Friedrich, P.; Linckens, A. *Synthesis* **1976**, 256. (b) Blankespoor, R. L.; Chung, C. S. C. *J. Org. Chem.* **1975**, *40*, 2443.

(20) Burgstahler, A. W.; Boger, D. L.; Naik, N. C. *Tetrahedron* **1976**, *32*, 309.

(21) (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7218

(22) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596.

(23) (a) Paquette, L. A.; Kravetz, T. M.; Hsu, L.-Y. *J. Am. Chem. Soc.* **1985**, *107*, 6598. (b) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1980**, *45*, 4907.

(24) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

(25) Nagarkatti, J. P.; Ashley, K. R. *Tetrahedron Lett.* **1973**, 4599.

(26) Williams, D. R.; Brown, D. L.; Benbow, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 1923.

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