Weiss–Cook Condensations Involving Unsaturated and Transannularly Alkylated Cyclododecane-1,2-diones

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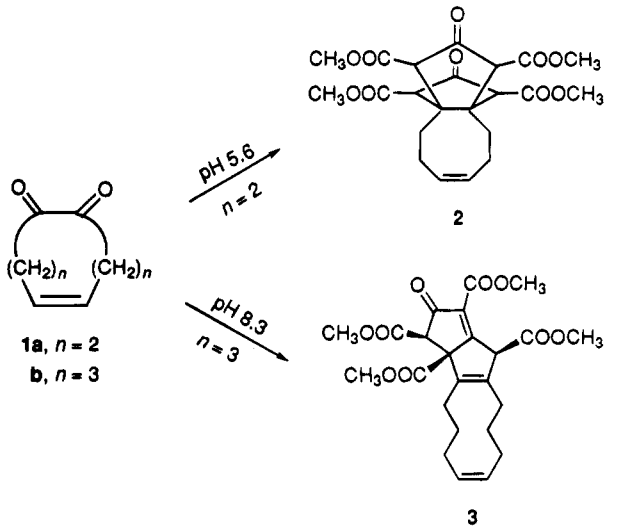
(*Z*)-Cyclododec-7-ene-1,2-dione (**4**), its alkyne equivalent **7**, and the structurally related propellane **14** have been subjected to condensation with dimethyl 1,3-acetonedicarboxylate. The α-diketones **4** and **7** undergo the Weiss–Cook condensation normally to deliver diquinane products in high yield. The sterically congested **14** showed no tendency to react. The underlying cause of the parallelism between eight- and twelve-membered rings and the contrasting behavior of cyclodecyl analogs is evaluated in terms of thermodynamic versus kinetic control.

Following the discovery by Weiss and Edwards that glyoxal is capable of condensation with dimethyl 1,3-acetonedicarboxylate in water at pH 5 to give a *cis*-bicyclo[3.3.0]octane-3,7-dione derivative,[2] this reaction has been broadly exploited by Weiss and Cook as a vehicle for the formation of multicyclic polyquinane systems.[3] The mild conditions presumably promote the sequential operation of aldol, Michael, and β-elimination reactions.[4] Although aliphatic 1,2-dicarbonyl compounds routinely enter effectively into this condensation, recent observations have indicated that 2-fold cyclopentannulation can be problematic when certain medium-ring α-diketones are subjected to comparable conditions. For example, although good yields (>80%) have been reported for the conversion of 1,2-cyclooctanedione and 1,2-cyclododecanedione into [*n*.3.3]propellanes,[5] 2-cyclodecanedione responds ineffectively (30%) and only when basic conditions are employed.[6] Still more striking have been the contrasting responses of **1a** and **1b**. At pH 5.6, the cyclooctene derivative is transformed without complication into **2** (86%).[7] The higher homolog **1b** fails to undergo the Weiss–Cook reaction under these conditions but leads instead to the abnormal product **3** (41%) in methanol at pH 8.3.[8] The formation of **3** has been linked to the thermodynamics peculiar to *cis*-cyclodecene and *cis,cis*-1,6-cyclodecadiene,[9] as well as to the notable nonbonded steric compression that is associated with ten-membered rings.[10]

No distinction has been made between the relative weighting of these two factors. In an effort to gain further insight into the principal control element crucial to the smooth operation of these cyclocondensations, we have now examined the reactivity of cyclododecane-1,2-diones structurally modified at the most remote C-7/C-8 positions of the ring.



Results

In the first series of experiments, the *Z*-enone **4**[11] was treated with dimethyl 1,3-acetonedicarboxylate and citrate–phosphate buffer (pH 5.6) in methanol at rt. During the course of 5 days, diketo tetraester **5** precipitated from the solution as a white solid (79%, Scheme 1). Subsequent acidic hydrolysis with decarboxylation produced diketone **6**.

The cycloalkynedione **7**, accessible as well by means of the Cram and Allinger protocol,[11] served more efficiently as a Weiss–Cook substrate. Under essentially the same reaction conditions, 2-fold annulation occurred to deliver **8** in very good yield (90%). The linkup of **8** with **6** could be accomplished either by semihydrogenation of **8** to **5** prior to decarboxylation or by a reversal of these two steps. The latter sequence also constitutes an attractive route to propellanedione **9**.

As a consequence of the above, it is clear that the pair of adjacent carbonyl groups in **4** and **7** are not disadvantaged with regard to entering into Weiss–Cook condensation. The observed reaction efficiencies compare favorably with that reported previously for cyclododecane-1,2-dione.[5]

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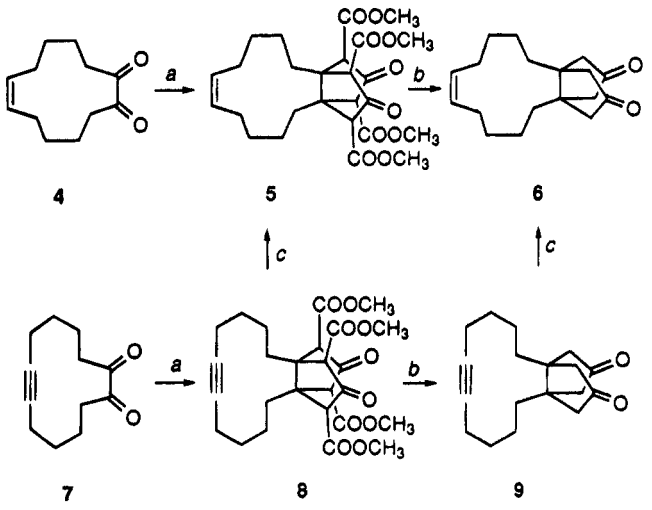
Scheme 1[a-c]



[a] Dimethyl 1,3-acetonedicarboxylate, citrate–phosphate buffer (pH 5.6), CH_3OH, 25 °C, 4–5 days. [b] HOAc, 1 M HCl, reflux. [c] 5% $Pb/BaSO_4$, H_2, quinoline, CH_3OH.

The effect of transannular steric compression was next probed by the further elaboration of **6** to give diketone **14** (Scheme 2). Following cis dihydroxylation of this enedione with catalytic OsO_4 in the presence of *N*-methylmorpholine *N*-oxide,[12] the hydroxyl groups were temporarily masked as the acetonide. With **11** in hand, reduction with $LiAlH_4$ and formation of bis-xanthate **12b** set the stage for implementation of a 2-fold Chugaev elimination. Thermal activation in this manner delivered diene **13a** as a 5:3 mixture of double-bond positional isomers. At this point, the acetal that had served us well was removed via acidic hydrolysis, and diol **13b** so produced was oxidized to give the desired α-diketone **14**. All attempts to induce **14** to undergo condensation with dimethyl 1,3-acetonedicarboxylate proved unsuccessful. The conditions examined embraced different solvents and a wide pH range from the strongly acidic to the strongly alkaline and many intermediate stages. Thus, the inertness of **14** is quite striking.

To our knowledge, heat of hydrogenation data are not available for the conversion of cyclododecene (**17**) and cyclododecyne (**18**) to cyclododecane (**16**). Effective use was therefore made of MM2 calculations[13] to locate the global minimum energy conformation of these and allied hydrocarbons, e.g. 1,7-cyclodecadiene (**19**), in order to gain some appreciation of their strain energies. Recourse was made to the statistical search method within the MODEL KS 2.99 program[14] because of the conformational mobility of the systems being studied. In the case of cyclododec-7-en-1-yne (**20**), direct comparison of the statistical search and grid search techniques proved possible, and identical results were realized. In those two instances where prior literature data are available, viz. for **16**[15] and **18**,[16] good matches were achieved.[17] The energy data, obtained by minimization within MMX of the best conformation in each instance, are compiled in Table 1.

Table 1. Energy Data for 16–20[a]

compd	ΔH_f	strain energy	total energy
16	−53.96	12.69	20.61
17	−28.06	10.80	16.90
18	8.59	8.84	14.94
19	−3.17	7.91	12.19
20	36.05	8.51	12.79

[a] All values are in kcal/mol.

This appraisal illustrates the favorable energy features associated with the introduction of double and triple bonds into large rings. The resultant diminution in nonbonded steric interactions is accompanied by a modest reduction in strain energy (E_s). The same trend is apparent in ten-membered rings, with 1,6-cyclododecadiene being 4.6 kcal/mol less strained than cyclodecene.[9] This trend is reversed, however, in eight-membered rings. Due to the limiting ring size in cyclooctyl systems, 1,5-cyclooctadiene (E_s = 8.2 kcal/mol) is more strained than cyclooctene (E_s = 4.9 kcal/mol).

However, as discussed above, cyclooctyl and cyclododecyl 1,2-dicarbonyl compounds enter normally into Weiss–Cook condensations. Cyclodecyl derivatives constitute the exception. Unfortunately, molecular mechanics calculations do *not* provide an explanation for these observations. In actuality, they suggest that **1b** and **4** should exhibit parallel behavior. This finding has led us to seek out a kinetic rather than a thermodynamic cause for the divergent behavior. Specifically, the conversion of **21** (n = 3) to **22** may be kinetically disadvantaged relative to that of the other examples because of rapid dehydration with introduction of a second double bond internal to the ring as defined in **24** (Scheme 3). Conversion to **3** would subsequently arise by 1,6-addition to the β-keto ester enolate. If this is so, the issue of thermodynamic versus kinetic control could gain importance and dictate the specific reaction outcome.

Experimental Section[18]

Tricyclo[10.3.3.0^{1,12}]octadec-6-ene-14,17-dione (6).[19] (*Z*)-Cyclododec-7-ene-1,2-dione (4.4 g, 22.7 mmol) was added to a mixture of dimethyl 1,3-acetonedicarboxylate (7.9 g, 45.4 mmol) and 50 mL of citrate–phosphate buffer. Following the introduction of methanol (80 mL) to achieve a clear solution, the reaction mixture was stirred for 5 days at rt and the white precipitate was filtered, washed with water, and dried to give 7.3 g (79%) of **5** as a white solid that was directly hydrolyzed.

A mixture of **5** (7.4 g, 15.4 mmol), glacial acetic acid (80 mL), and 10% hydrochloric acid (80 mL) was refluxed for 6 h, cooled, and diluted with water to 300 mL. Chloroform (50 mL) was added followed by solid $NaHCO_3$ until pH 7 was reached. The mixture was extracted with $CHCl_3$ (4×), and the combined organic layers were washed with water and brine prior to drying and solvent evaporation. The residue was recrystallized from hexanes to give 3.1 g (73%) of **6** as a white solid, mp 101–102 °C (from hexanes): IR (CCl_4, cm^{-1}) 1750; ^1H NMR

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(14) We thank Professor K. Steliou for making this program available to us.

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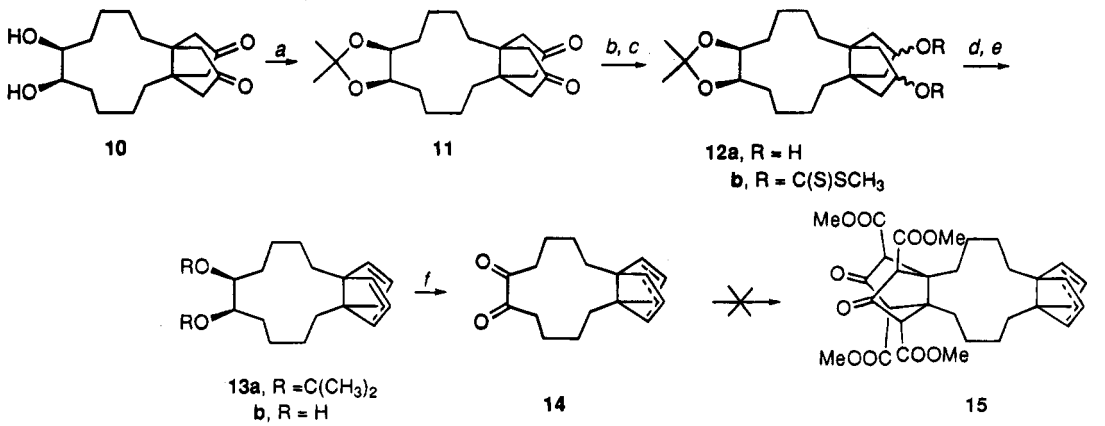
(18) For general information, see: Paquette, L. A.; Schulze, M. M.; Bolin, D. G. *J. Org. Chem.* **1994**, *59*, 2043.

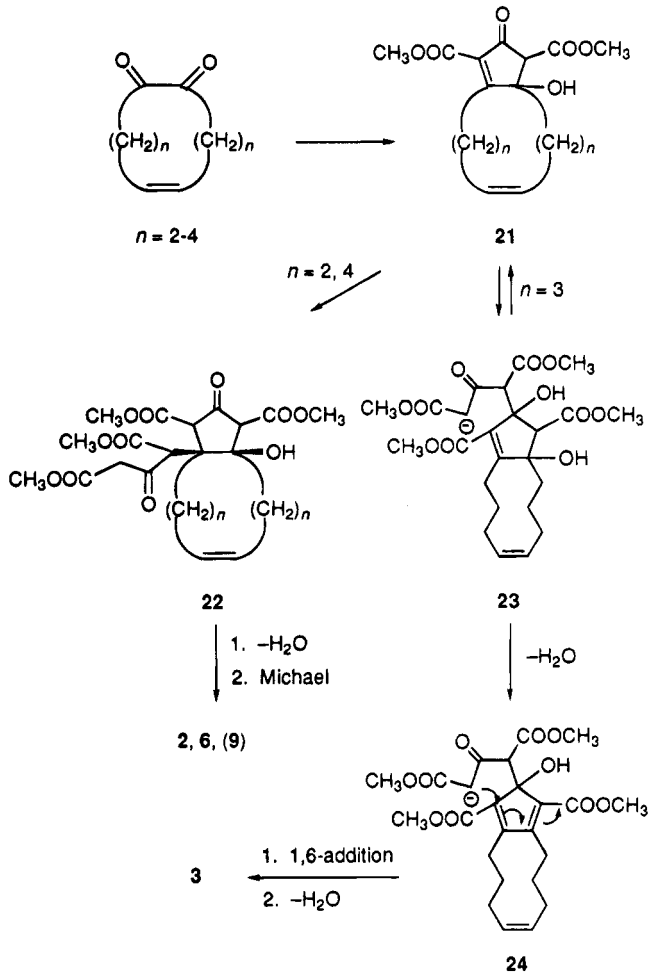
(19) This experiment was first performed by Dr. Gail Underiner.

Scheme 2[a–f]



[a] Acetone, (TsOH), rt. [b] $LiAlH_4$, THF, 0 °C. [c] NaH, CS_2, THF; CH_3I. [d] 200–210 °C, 1 h. [e] CH_3OH, (TsOH), reflux. [f] $(COCl)_2$, DMSO, CH_2Cl_2; Et_3N.

Scheme 3



(300 MHz, $CDCl_3$) δ 5.30 (t, J = 5.0 Hz, 2 H), 2.41 (d, J = 19.3 Hz, 4 H), 2.27 (d, J = 19.3 Hz, 4 H), 2.40–2.00 (series of m, 4 H), 1.63–1.25 (series of m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 216.9, 103.8, 51.7 (2C), 48.2, 33.9, 26.7, 25.0, 22.7; MS m/z (M^+) calcd 274.1933, obsd 274.1936.

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.77; H, 9.65.

Tricyclo[10.3.3.0^{1,12}]octadec-6-ene-14,17-dione (9). A solution of **7** (930 mg, 4.85 mmol) in methanol (40 mL) was added to 20 mL of citrate–phosphate buffer (pH 5.6). After 1.72 g (9.7 mmol) of dimethyl 1,3-acetonedicarboxylate was introduced, the mixture was stirred at rt for 4 days. The white precipitate was filtered, washed with cold methanol–water (1:1), and dried in vacuo over P_2O_5 to give 2.24 g (90%) of **8** as a white solid that was directly hydrolyzed.

A solution of **8** (200 mg, 0.389 mmol) in glacial acetic acid (20 mL) and 1 M hydrochloric acid (20 mL) was refluxed for 6 h, cooled, diluted with $CHCl_3$, and neutralized with solid $NaHCO_3$. Threefold extraction with $CHCl_3$ was followed by washing of the combined organic layers with brine, saturated $NaHCO_3$ solution, and brine. After drying and solvent evaporation, the residue was recrystallized from methanol to give **9** (74 mg, 76%) as colorless prisms, mp 101 °C: IR (KBr, cm^{-1}) 1744; ^1H NMR (300 MHz, $CDCl_3$) δ 2.47 (d, J = 19.5 Hz, 4 H), 2.31 (d, J = 19.5 Hz, 4 H), 2.25 (m, 4 H), 1.98 (m, 4 H), 1.51 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 216.9, 82.3, 51.2 (2C), 48.8, 35.4, 26.3, 24.0, 18.3; MS m/z (M^+) calcd 272.1776, obsd 272.1774.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.07; H, 8.93.

Hydrogenation of 8. To a solution of **8** (200 mg, 0.389 mmol) in THF (30 mL) and MeOH (20 mL) were added 8 mg of 5% palladium on barium sulfate and 8 mg of quinoline. The mixture was hydrogenated over 1 atm of H_2 for 20 min, filtered, and freed of solvent. The resultant **5** was directly decarboxylated as detailed above to give 92 mg (87% overall) of **6**.

Hydrogenation of 9. A 704 mg (2.54 mmol) sample of **9** was dissolved in methanol (10 mL), treated with 20 mg of 5% palladium on barium sulfate and 25 mg of quinoline, and hydrogenated at atmospheric pressure for 18 h. After filtration and solvent evaporation, pure diketone **6** was obtained (658 mg, 93%).

***meso*-Decahydro-2,2-dimethyl-7a,10a-propano-8*H*-cyclopenta[7,8]cyclododeca[1,2-*d*]-1,3-dioxole-9,16(10*H*)-dione (11).** *N*-Methylmorpholine *N*-oxide (7.73 g, 66.2 mmol) and a crystal of OsO_4 were added to a solution consisting of THF (90 mL), *tert*-butyl alcohol (80 mL), and water (10 mL). This mixture was cooled to 0 °C, and a solution of **6** (12.1 g, 44.1 mmol) in THF (50 mL) was added. After 3 days of stirring at rt, an additional gram of NMO and small crystal of OsO_4 were introduced. Reaction was allowed to proceed for a total of 6 days, at which point a saturated solution of $NaHSO_3$ was added. After 30 min of vigorous agitation, the solvent was evaporated. The residue was triturated 15 times with hot ethyl acetate, and the combined extracts were washed with brine, dried, and evaporated. Recrystallization of the residue from hexanes–ethyl acetate afforded 10.4 g (77%) of **10** which was directly converted to **11**.

A solution of unpurified **10** (730 mg) and *p*-toluenesulfonic acid (30 mg) in acetone (20 mL) was stirred at rt for 36 h and concentrated under reduced pressure. The residue was recrystallized from ether or chloroform-hexanes to give a white crystalline solid, mp 83–85 °C: IR (KBr, cm^{-1}) 1747; ^1H NMR (300 MHz, $CDCl_3$) δ 4.01 (t, J = 3.2 Hz, 2 H), 2.51 (d, J = 18.8 Hz, 2 H), 2.40 (d, J = 19.0 Hz, 2 H), 2.30 (d, J = 19.6 Hz, 4 H), 1.92–1.39 (series of m, 14 H), 1.45 (s, 3 H), 1.34 (s, 3 H), 1.31–1.18 (m, 2 H); MS m/z (M^+) calcd 348.2301, obsd 348.2288.

Anal. Calcd for $C_{21}H_{32}O_4$: C, 72.39; H, 9.26. Found: C, 72.39; H, 9.32.

***cis*-4,5,6,7,8,9,10,11,12,13-Decahydro-8,9-diisopropoxy-3a,13a(and 13a,3a)-propeno-1*H*-cyclopentacyclododecene (13a).** A solution of **11** (400 mg, 1.15 mmol) in THF (20 mL) was added dropwise to a stirred slurry of lithium aluminum hydride (200 mg, 5.27 mmol) in THF (25 mL) at 0 °C. The mixture was allowed to warm to rt during 30 min, at which point 1 mL of saturated Seignette salt solution was added. The precipitate was separated by filtration, dissolved in water, and extracted with ethyl acetate (3×). The combined organic layers were washed with brine (2×), dried, and concentrated. Chromatography of the residue on silica gel (elution with 6:1 hexanes–isopropyl alcohol) and recrystallization from ethyl acetate gave 373 mg (92%) of **12a** as a white solid, mp 125 °C: IR (KBr, cm^{-1}) 3325; ^1H NMR (300 MHz, $CDCl_3$) δ 4.60–4.1 (m, 2 H), 4.1–3.97 (m, 2 H), 2.2–1.25 (series of m, 26 H), 1.45 (s, 3 H), 1.37 (s, 3 H); MS *m/z* (M^+) calcd 352.2614, obsd 352.2610.

A 1.77 g sample (5.02 mmol) of **12a** in THF (50 mL) was added dropwise to a magnetically stirred mixture of sodium hydride (1 g, 41.6 mmol) in carbon disulfide (70 mL), heated at reflux for 45 min, cooled to rt, and treated with methyl iodide (15 mL, 240 mmol). This reaction mixture was refluxed for 30 min, stirred overnight at rt, treated cautiously with water, and extracted with ether (5×). The combined organic layers were washed with water and brine (2×), dried, and evaporated to leave a yellow oil which was blanketed with N_2 and immersed in a hot (200–210 °C) oil bath for 1 h. The cooled residue was taken up in hexanes–ethyl acetate (20:1), chromatography on silica gel, and recrystallized from isopropyl alcohol–methanol to give **13a**, a colorless solid, mp 83–85 °C, as a 5:3 mixture of double-bond isomers (1.29 g, 80%): IR (KBr, cm^{-1}) 3060, 1625, 1615; ^1H NMR (300 MHz, $CDCl_3$) δ 5.58 (m, 2 H), 5.44 (m, 1 H), 5.32 (m, 1 H), 4.17 (m, 1 H), 4.04 (m, 1 H), 2.35–2.10 (m, 4 H), 1.44 (s, 3 H), 1.33 (s, 3 H), 1.95–1.05 (series of m, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.4, 139.7, 137.0, 135.5, 128.1, 127.7, 126.7, 126.2, 106.2, 106.1, 80.5, 78.9, 78.4, 77.7, 66.6, 60.0, 58.5, 53.5, 47.7, 45.6, 45.1, 44.6, 34.4, 33.8, 33.3, 31.4, 28.9, 28.54, 28.50, 26.4, 26.2, 26.1 (2C), 26.0, 25.9, 25.5, 24.8 (2C), 21.9, 21.7; MS *m/z* (M^+) calcd 316.2402, obsd 316.2402.

Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.66; H, 10.24.

***cis*-4,5,6,7,8,9,10,11,12,13-Decahydro-3a,13a(and 13a,-3a)-propeno-1*H*-cyclopentacyclododecene-8,9-diol (13b).** A solution of **13a** (340 mg, 1.1 mmol) and *p*-toluenesulfonic acid (40 mg) in 90% methanol (150 mL) was refluxed overnight, cooled, treated with saturated $NaHCO_3$ solution, and evaporated. The residue was extracted with ethyl acetate, and the product was purified by silica gel chromatography (elution with 2:1 hexanes–ethyl acetate) to give 279 mg (92%) of **13b** as a white crystalline solid, mp 125 °C (from ether): IR (KBr, cm^{-1}) 3360; ^1H NMR (300 MHz, $CDCl_3$) δ 5.61, 5.52, and 5.40 (m's, total of 4 H), 3.78 (m, 2 H), 2.4–2.1 (series of m, 6 H), 1.75–1.2 (series of m, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.2, 139.4, 137.2, 134.7, 128.6, 127.0, 126.9, 125.7, 75.1, 74.32, 74.28, 72.5, 66.7, 60.3, 58.4, 53.9, 46.3, 44.8, 44.3, 42.0, 33.8 (2C), 33.4, 31.0, 29.3, 29.0, 27.6, 26.7, 24.2, 24.1, 23.9, 23.5, 23.3, 23.1, 22.8, 21.9; MS *m/z* (M^+) calcd 276.2089, obsd 276.2088.

Anal. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 77.81; H, 10.37.

4,5,6,7,10,11,12,13-Octahydro-3a,13a(and 13a,3a)-propeno-1*H*-cyclopentacyclododecene-8,9-dione (14). A cold (−78 °C), magnetically stirred solution of oxalyl chloride (331 mg, 2.71 mmol) in CH_2Cl_2 (10 mL) was treated with dry DMSO (260 mg, 3.3 mmol) and, 5 min later, with a solution of **13b** (340 mg, 1.24 mmol) in CH_2Cl_2 (5 mL) over a period of 5 min. The mixture was stirred at −78 °C for 1 h, treated with triethylamine (700 mg, 6.91 mmol), and allowed to warm to rt. The solvent was evaporated, and the residue was taken up in ether, filtered, and concentrated in vacuo. The resulting yellow oil was chromatographed on silica gel (elution with 20:1 hexanes–ethyl acetate) to give 200 mg (60%) of **14** (a 1.6:1 isomer mixture) as a white crystalline solid, mp 48.5 °C (from hexanes): IR (KBr, cm^{-1}) 1703, 1445, 1425, 1333, 955, 745, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 5.57 (m, 2 H), 5.42 (m, 2 H), 3.32 (ddd, J = 2.8, 12.7, 15.5 Hz, 1 H), 2.83 (m, 1 H), 2.71 (m, 1 H), 2.26 (m, 3 H), 2.13 (m, 2 H), 1.80 (m, 4 H), 1.30 (m, 6 H), 1.05 (m, 1 H), 0.85 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 202.1, 202.0, 201.8, 138.9, 135.5, 127.9, 127.0, 66.8, 59.1, 53.3, 45.6, 43.8, 35.5, 34.6, 33.2, 32.4, 31.8, 31.4, 26.3, 24.9, 24.5, 23.7, 23.5, 22.0; MS *m/z* (M^+) calcd 272.1776, obsd 272.1774.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 78.90; H, 8.82.

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Supplementary Material Available: Final computed atomic coordinates for **16–20** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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