

Chemistry of cage-shaped hydrocarbons. Reactions of pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane-4,11-diene

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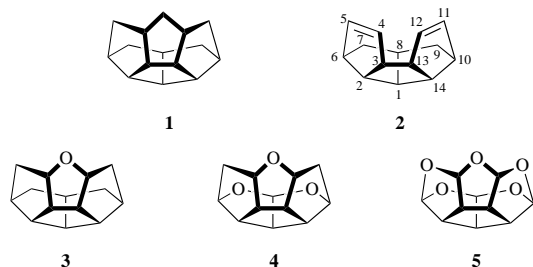
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A formal synthesis of peristylane **1** and oxaperistylane **3** are accomplished through chemical modifications of a cage-shaped molecule pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane-4,11-diene **2**. Reaction of **2** with NBS resulted in the formation of two dibromides **7** and **9** and a bromohydrin **8**. Compound **9** was derived from **8** through bromination followed by a transannular ring closure. Epoxidation of **2** with MCPBA produced an epoxide **15** and a diepoxide **13**, both with the oxygen atoms oriented on the *exo*-side of the rings. Hydroboration of **2** followed by oxidation yielded a mixture of three isomeric diketones **20**, **21** and **22**. Oxaperistylane **3** was obtained from **21** by two successive reduction reactions. Peristylane **1** can be prepared from **22** by a known procedure. The structures of **9** and **20** were characterized by single crystal X-ray diffraction analyses.

Introduction

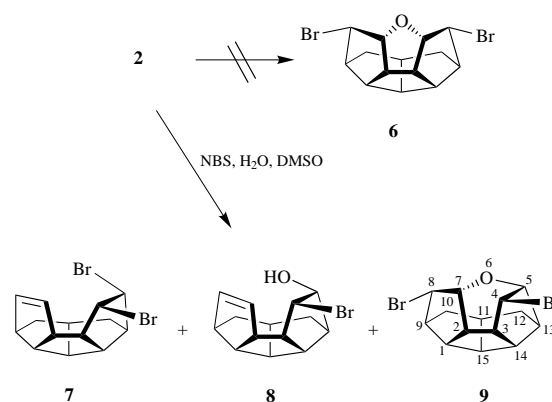
The five-fold symmetrical structure of peristylane **1** has been regarded as a key intermediate in the synthesis of dodecahedrane.¹⁻⁴ It was first prepared by Eaton *et al.* in 1977 through a multi-step synthetic sequence.⁵ The major stereochemical challenge in the preparation was to fuse a series of five-membered rings all in a cisoid manner. The difficulty of preparation on a large scale therefore limits its availability for potential applications.^{6,7} This problem may now be partly solved by the recent discovery of an effective catalytic system which converts norbornadiene (NBD) directly to an all cisoid-fused pentaquinadiene **2** in excellent yield.⁸ The structure of **2** has all the correct features suitable for a convenient preparation of **1**, and in this report some oxidative reactions of **2** are examined. Along with **1**, an oxaperistylane **3** was also obtained, which belongs to the group of oxygenated peristylanes such as **4** and **5**. This series of molecules has attracted considerable attention in recent years due to their crown ether-like geometries.⁹



Results and discussion

Reaction with NBS

Diene **2** was treated with *N*-bromosuccinimide (NBS) in an attempt to make **6**. Three products were isolated from the reaction after 4 hours and were identified as compounds **7** (30%), **8** (10%) and **9** (40%) (Scheme 1). The NMR spectra of both **7** and **8** show the presence of an olefinic bond, whereas that of **9** indicates the presence of an etheral linkage. The lack of planar

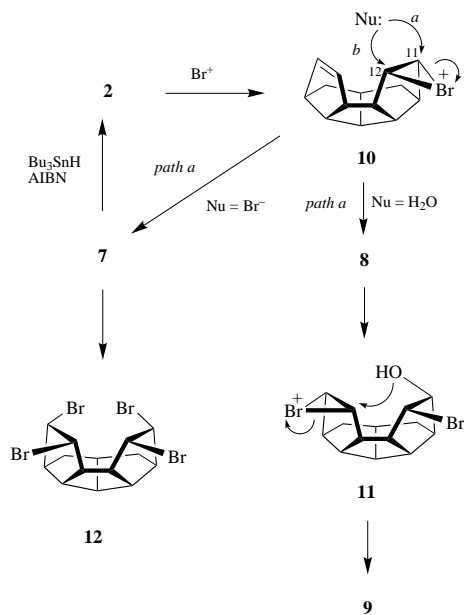


Scheme 1

symmetry for **9** distinguishes it from **6**. The stereochemistry of **7** and **8**, however, cannot be determined unambiguously by NMR spectral data, which are assigned later by comparison with known structures.

The reaction mechanism was believed to proceed through a bromonium ion **10** (Scheme 2), which was attacked either by a bromide ion to form **7** or by a water molecule to form **8**. Subsequent bromination on the double bond of **8** yielded **9**, presumably going through another bromonium ion **11**. The relative yield of **8** to **9** therefore depends on the time of reaction, but that of **7** with respect to (**8** + **9**) should be invariant with time as depicted. In Table 1 the yields of **7**, **8** and **9** are measured with various amounts of NBS at different reaction times. Within the limits of experimental error, it is quite clear that the yield of **9** increases at the expense of **8**. Compound **8** can be isolated in appreciable amounts only at the early stages of the reaction. In a controlled experiment, **8** was converted to **9** quantitatively upon treatment with NBS.

The stereochemistry of **7** and **8** can be rationalised by a closer look at the mechanism (Scheme 2). Both compounds were formed by nucleophilic attack on one of the two carbons, *i.e.* C(11) and C(12). It appears that **9** may be derived from **10** either through **8** (*path a*) or through an isomer of **8** with the hydroxy group attached to C(12) (*path b*). Steric hindrance



Scheme 2

Table 1 Isolated yields of products in the reaction of **2** with NBS

Molar equiv. of NBS	Reaction time/h	Yield (%)			Recovered 2 (%)
		7	8	9	
1.1	0.5	28	13	27	30
3.0	4	30	10	39	10
3.0	7	34	5	36	10
6.7	20	27	0	40	10

around C(11) seems to be less severe than around C(12), therefore *path a* is preferred to *path b*. The stereochemistry of **7** can be assigned by analogy with the structure of tetrabromide **12**, the geometry of which has been confirmed by crystallography.⁸ The stereochemistry of **8** should be similar to that of **7**, assuming the steric requirement for a bromide, acting as a nucleophile, is similar to that of a hydroxide. Further evidence supporting our assignment of the structure of **8** is based on that of **9**. If the hydroxy group of **8** is located at C(12) instead of at C(11), subsequent ring closure would yield both **9** and **6** since the strain energies estimated for both compounds are close to each other, *i.e.* 43.3 kcal mol⁻¹ for **9** vs. 44.4 kcal mol⁻¹ for **6** by MM2(91).¹⁰ But as we have mentioned earlier, **9** was observed exclusively without **6**.

Reduction of **7** with tributyltin hydride in the presence of AIBN regenerated **2** in good yield. Compound **2** thus obtained was stable for several days at room temperature.⁸ The structure of **9** was determined by X-ray diffraction analysis on a single crystal.† An ORTEP drawing is shown in Fig. 1 indicating the *exo*-orientation of the bromine atoms. The C–C bonds adjacent to a C–Br group are relatively shorter than others as predicted by Bent's rules.¹¹ The higher electronegativity of the bromine atom results in a higher p-character for the hybridization of the carbon atom of the C–Br bond, which results in more s-character distributed between the other two C–C bonds. The average distance of C(5)–C(6), C(6)–C(7), C(9)–C(10) and C(10)–C(11) is 1.52(1) Å, whereas the rest average 1.54(1) Å. Crystal data for **9** are listed in Table 2.

† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available via the RSC Web pages (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/185.

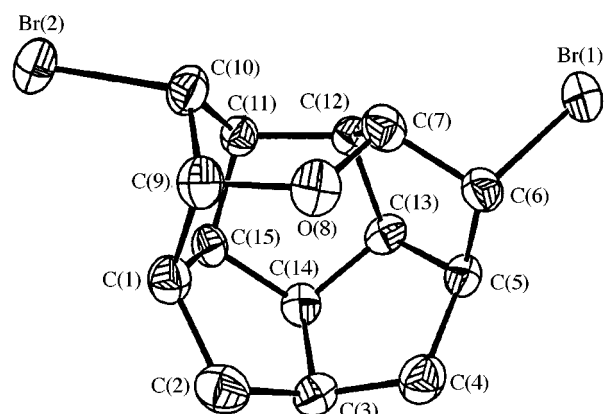
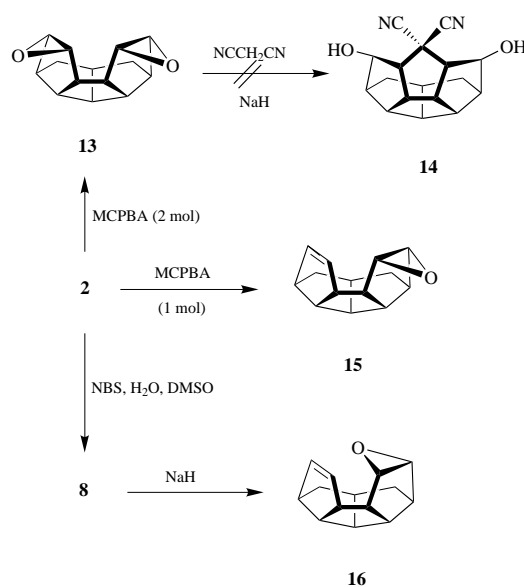


Fig. 1 Molecular structure of **9**. Hydrogens are omitted for clarity

Formal syntheses of **1** and **3**

Peristylane **1** is derived from **2** by formal addition of a methylene unit between C(4) and C(12). A conversion of **2** to **14** has been considered by going through a diepoxide intermediate **13**. Compound **13** was obtained readily from **2** by reacting with two molar equivalents of MCPBA. However, treatment of **13** with the anion of malononitrile (NCCH₂CN with NaH) did not yield the desired adduct **14** (Scheme 3). The nucleophile seems



Scheme 3

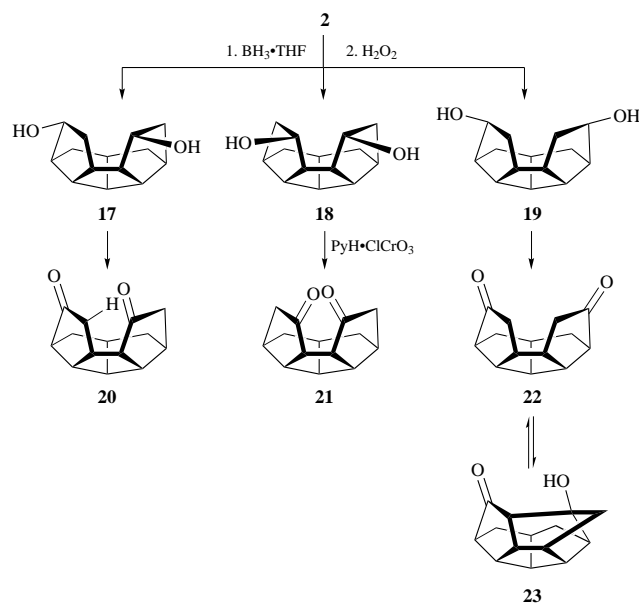
to be too bulky to attack from the *endo* sides of the concave **13** if the oxygen atoms are oriented on the *exo* faces. The orientation of the epoxy rings is unambiguously established by comparison between the two stereoisomers **15** and **16**. Dehydrobromination of **8** with NaH yielded an *endo*-epoxide **16** which shows different spectroscopic character from that of the *exo*-isomer **15**. The latter was prepared independently by a reaction of **2** with one molar equivalent of MCPBA (Scheme 3).

The diene **2** was converted to the diols **17**, **18** and **19** through a hydroboration sequence (BH₃·THF followed by basic H₂O₂). The relative yield of **17**:**18**:**19** was roughly 2:1:1 indicating the lack of regioselectivity between the two olefinic carbons (Scheme 4). The ¹³C NMR spectra of both **18** and **19** show 8 signals reflecting their two-fold symmetries, whereas that of **17** shows 14 peaks in the absence of such symmetry. The three diols were purified and oxidized separately by pyridinium dichromate to the corresponding diketones **20**, **21** and **22** in yields of *ca.* 80%. Among the three diketones only one possesses a two-fold symmetry in the NMR spectra; its structure was later confirmed to be that of **21**. A rearrangement of diketone **22** to **23** occurs readily in chloroform (Scheme 4).¹² Force-

Table 2 Crystallographic and refinement data for compounds **9** and **20**

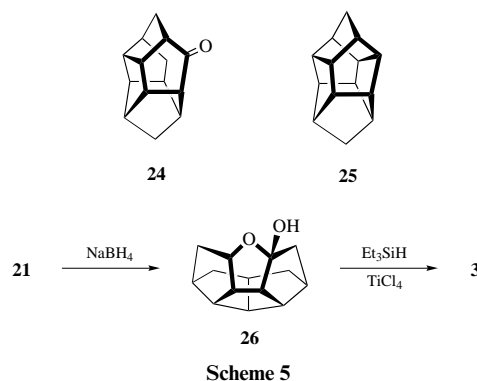
Compound	9	20
Empirical formula	C ₁₄ H ₁₆ Br ₂ O	C ₁₄ H ₁₆ O ₂
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> <i>c</i>
Cell dimensions		
<i>a</i> /Å	6.1334(6)	7.484(1)
<i>b</i> /Å	8.5606(5)	13.141(3)
<i>c</i> /Å	23.208(2)	11.165(2)
β (°)	91.276(7)	101.71(3)
<i>V</i> /Å ³	1218.3(2)	1075.3(3)
Crystal size/mm	0.41 × 0.38 × 0.31	0.46 × 0.46 × 0.38
Formula weight	360.09	216.27
<i>Z</i>	4	4
<i>F</i> (000)	712	464
<i>D</i> /g cm ⁻³	1.963	1.330
μ /mm ⁻¹	1.32	0.088
λ /Å	0.7107	0.7107
2 θ (max)	50.0	45
Diffractometer	Nonius CAD-4	Nonius CAD-C
Scan mode	θ -2 θ	θ -2 θ
<i>hkl</i> mode	-7 < <i>h</i> < 7, 0 < <i>k</i> < 10, 0 < <i>l</i> < 27	-8 < <i>h</i> < 7, 0 < <i>k</i> < 14, 0 < <i>l</i> < 11
No. unique reflexes	2144	798
No. obsns <i>I</i> _o > 2 σ (<i>I</i> _o)	1460	695
Transmission factors	0.53–1.00	0.88–0.98
Parameters	155	209
<i>R</i> ^a	0.042	0.0273
<i>R</i> _w	0.042 ^b	0.0757 ^c
Goodness of fit	1.88 ^d	0.969 ^e
Maximum Δ/σ	0.003	0.001
D-map maximum, e Å ⁻³	0.830	0.109
D-map minimum, e Å ⁻³	-0.730	-0.089

^a $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^b $[w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. ^c $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w|F_o|^2]^{1/2}$. ^d $[\Sigma w(|F_o| - |F_c|)^2/(m - p)]^{1/2}$. ^e $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(m - p)\}^{1/2}$.

**Scheme 4**

field calculations [MM2(91)] confirm that the heat of formation of **23** (-113.8 kcal mol⁻¹) is lower than that of **22** (-104.3 kcal mol⁻¹), although the strain of the former (44.0 kcal) is higher than that of the latter (34.9 kcal).¹⁰ The skeleton of **23** is analogous to that of **24**, which has been prepared by us previously from **25** and whose chemistry has been studied thoroughly.^{13,14} The pentacyclic dione **22** has been previously transformed into **1** in five steps (*ca.* 60% yield) thus constituting a formal synthesis of 5-peristylane.^{5,12}

The oxaperistylane **3** was obtained by reduction of **21** with NaBH₄, followed by Et₃SiH-TiCl₄ (Scheme 5). In this sequence **26** was isolated as an intermediate, whose structure was identified by spectroscopic data. The hemiketal form of **26** is stable and resistant to further reduction by sodium borohydride.

**Scheme 5**

Compound **3** shows eight absorptions in the ¹³C NMR spectrum and gives a parent peak corresponding to its molecular ion in the mass spectrum.

Structural analysis

Transannular interaction is a common phenomenon in this series of molecules.¹³ In the ¹H NMR spectrum of **20**, an unusually high field absorption is observed at δ 0.50. This signal derives from one hydrogen atom of a -CH₂- moiety where the other one appears at δ 1.95. The coupling pattern looks like a quartet but should be a ddd (three doublets) with the three *J* values nearly equivalent (11 ~ 12 Hz). Based on these characteristics, we believe that this signal is derived from *endo*-H(7), which is shielded by the proximate carbonyl groups. In order to eliminate any ambiguities, the single crystal structure of **20** was determined by X-ray diffraction analysis. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on difference Fourier maps and were refined isotropically.¹⁵ An ORTEP drawing of **20** is shown in Fig. 2, in which one can observe that the *endo*-H(7a) is located within the shielding cone region of both the two C=O groups. The conformation of CH₂(7), unlike CH₂(9), tilts inward to the center of the cavity. The distances of *endo*-H(7a)-C(11) and *endo*-H(7a)-C(4) are

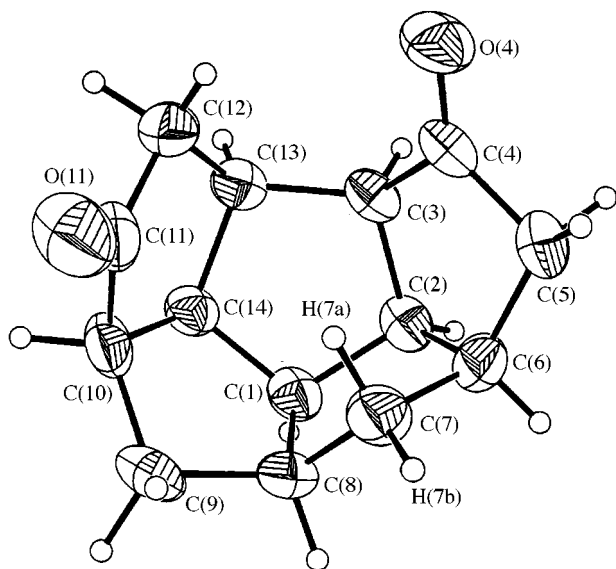


Fig. 2 Molecular structure of **20**. The *endo*-hydrogen on C(7), H(7a), is located within the shielding region of C(11)=O(11) and C(4)=O(4). H(7a)–C(11) and H(7a)–C(4) distances are 2.62(5) Å and 2.70(5) Å respectively

2.62(5) Å and 2.70(5) Å respectively. The bonds attached to carbonyl groups are apparently shorter than others. The average distance of C(3)–C(4), C(4)–C(5), C(10)–C(11) and C(11)–C(12) is 1.502(5) Å, whereas the rest average to 1.530(5) Å. Crystal data for **20** are listed in Table 2.

Conclusion

Peristylane **1** and oxaperistylane **3** can be readily obtained starting from compound **2**. In most of the oxidation reactions, however, regioselectivity among the olefinic carbons is quite low. Due to the closeness of functional groups inside the concave face of the cage-shaped molecules, transannular interactions are observed among this series of compounds.

Experimental

¹H and ¹³C NMR spectra were obtained on either a Bruker AC-200 or AC-300 FT spectrometer. Chemical shifts of ¹H were measured downfield from TMS in δ units, while those of ¹³C were recorded with the central peak of CDCl₃ at δ 77.00 as an internal reference. *J* Values are given in Hz. Infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. Elemental analyses were obtained on a Perkin-Elmer 2400 EA instrument. Mass spectra were carried out on a VG Analytical 70-250 S/SE spectrometer. Melting points were measured by a Yanaco MICRO mp apparatus model MP-S3 and were uncorrected.

2-Oxahexacyclo[7.5.1.0^{3,13}.0^{5,12}.0^{7,11}.0^{10,14}]pentadecane (oxaperistylane) **3**

To a solution of **26** (0.22 g, 1.00 mmol) in CH₂Cl₂ (20 cm³) was added triethylsilane (0.35 g, 3.0 mmol) and TiCl₄ (20 mg, 0.10 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 0.5 h, then was quenched by the addition of water (10 cm³). The resulting mixture was extracted with CH₂Cl₂ (20 cm³ × 3), washed with brine, dried over anhydrous MgSO₄, and concentrated *in vacuo*. Compound **3** (190 mg, 0.92 mmol, 92% yield) was purified by a silica gel column chromatograph as a white waxy solid, mp 145–147 °C (Found M⁺, 202.1358. C₁₄H₁₈O requires *M*, 202.1358); ν_{max}(CHCl₃)/cm^{–1} 2935, 1099, 1044; δ_H(CDCl₃, 200 MHz) 2.18–2.22 (m, 8H), 2.40–2.80 (m, 3H), 3.05–3.25 (m, 5H), 4.37 (dd, *J* 5, 5, 2H); δ_C(CDCl₃, 50 MHz, ¹H-decoupled) 42.05, 43.72, 47.41,

48.29, 61.46, 62.55, 62.83, 90.30; *m/z* (EI, 50 eV) 202 (M⁺, 100%).

Reaction of **2** with NBS. 11,12-Dibromopentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecan-4-ene **7**, 12-bromopentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecan-4-en-11-ol **8** and 4,8-dibromo-6-oxahexacyclo[7.6.0.0^{2,7}.0^{3,14}.0^{5,13}.0^{11,15}]pentadecane **9**

Diene **2** (0.50 g, 2.7 mmol) was dissolved in DMSO (5.0 cm³) and water (0.5 cm³) in a round bottomed flask under nitrogen atmosphere. The solution was stirred with a magnetic bar at room temperature, and to it was added NBS (0.53 g, 3.0 mmol). The reaction was allowed to proceed for 0.5 h, then it was quenched by the addition of water. The products were extracted twice with CH₂Cl₂, washed once with brine, dried over anhydrous MgSO₄, and concentrated *in vacuo*. Compounds **7** (180 mg, 0.52 mmol, 28%), **8** (67 mg, 0.24 mmol, 13%) and **9** (180 mg, 0.50 mmol, 27%) were collected as colorless solids from a silica gel column chromatograph eluted with hexane: ethyl acetate (50:1). Physical data of **7**: mp 81–83 °C (Found C, 49.41; H, 4.72. C₁₄H₁₆Br₂ requires C, 49.13; H, 4.72%); ν_{max}(KBr)/cm^{–1} 3040, 2948, 1456, 1309, 1198; δ_H(CDCl₃, 400 MHz) 1.04–1.24 (q, *J* 12, 1H), 1.81–1.96 (m, 3H), 2.34–2.70 (m, 2H), 3.01–3.30 (m, 4H), 3.44–3.52 (m, 2H), 4.05–4.14 (dd, *J* 7, 10, 1H), 4.26–4.33 (dd, *J* 6, 10, 1H), 5.44–5.47 (dd, *J* 2, 5, 1H), 5.78–5.81 (dd, *J* 2, 5, 1H); δ_C(CDCl₃, 100 MHz, ¹H-decoupled) 36.5, 36.8, 47.8, 52.2, 53.6, 54.6, 56.4, 58.1, 58.2, 58.5, 59.9, 61.5, 128.6, 139.5; *m/z* (EI, 70 eV) 344 (M⁺, 4%), 263 (10), 183 (100), 141 (18), 117 (74). Physical data of **8**: ν_{max}(KBr)/cm^{–1} 3400, 2939, 1709, 1640, 1272, 1092; δ_H(CDCl₃, 200 MHz) 1.00–1.25 (q, *J* 12, 1H), 1.70–2.22 (m, 4H), 2.30–2.57 (m, 2H), 2.97–3.05 (m, 4H), 3.05–3.25 (m, 1H), 3.39–3.48 (m, 2H), 3.94–4.02 (dd, *J* 6, 9, 1H), 4.28–4.36 (dd, *J* 6, 9, 1H), 5.43–5.46 (dd, *J* 2, 5, 1H), 5.73–5.76 (dd, *J* 2, 5, 1H); δ_C(CDCl₃, 50 MHz, ¹H-decoupled) 33.4, 37.0, 48.8, 49.3, 53.6, 54.4, 55.1, 57.0, 57.5, 58.0, 59.3, 84.4, 128.8, 138.9; *m/z* (EI, 70 eV) 281 (M⁺ + 1, 3%), 280 (3), 263 (16), 197 (9), 183 (13). Physical data of **9**: mp 142–144 °C (Found C, 46.70; H, 4.42. C₁₄H₁₆Br₂O requires C, 46.93; H, 4.50%); ν_{max}(KBr)/cm^{–1} 2911, 1461, 1300, 1184, 1060, 1019; δ_H(CDCl₃, 200 MHz) 1.68–1.71 (m, 1H), 1.79–1.90 (m, 1H), 2.00–2.18 (m, 1H), 2.39–2.58 (m, 1H), 2.81–3.19 (m, 4H), 3.23–3.45 (m, 4H), 4.12 (d, *J* 4, 1H), 4.19 (d, *J* 3, 1H), 4.23 (s, 1H), 4.74 (m, 1H); δ_C(CDCl₃, 50 MHz, ¹H-decoupled) 36.6, 45.9, 49.8, 50.5, 54.6, 55.1, 56.7, 57.8, 58.1, 59.6, 60.0, 63.9, 78.4, 82.2; *m/z* (EI, 70 eV) 360 (M⁺, 41%), 358 (21), 362 (20), 279 (100), 261 (44), 199 (75), 171 (95).

Epoxidation of **2**. 4,5:11,12-Diepoxy-pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane **13** and 11,2-epoxypentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradec-4-ene (*exo*-isomer **15** and *endo*-isomer **16**)

Diene **2** (0.90 g, 4.9 mmol) was dissolved in freshly distilled CH₂Cl₂ in a round bottomed flask fitted with nitrogen inlet and outlet. To the solution was added MCPBA (1.95 mg, 11.3 mmol), and the resulting mixture was stirred under nitrogen atmosphere at 0 °C for 5 h. It was quenched with saturated aqueous Na₂S₂O₃, washed twice with saturated aqueous Na₂CO₃ and once with brine, dried over anhydrous MgSO₄, filtered and concentrated *in vacuo*. Diepoxide **13** was collected through a silica gel chromatograph eluted with hexane:ethyl acetate (6:1) to give a colorless solid in 62% yield (0.66 g, 3.0 mmol), mp 196–198 °C (Found: C, 77.72; H, 7.49. C₁₄H₁₆O₂ requires C, 77.74; H, 7.46%); ν_{max}(KBr)/cm^{–1} 2939, 1456, 1396, 1263, 1023; δ_H(CDCl₃, 200 MHz) 1.40–1.52 (m, 2H), 1.81–1.96 (m, 2H), 2.56–2.71 (m, 3H), 2.95 (br, 5H), 3.42 (d, *J* 2, 2H), 3.54 (d, *J* 2, 2H); δ_C(CDCl₃, 50 MHz, ¹H-decoupled) 35.9, 48.4, 49.4, 49.7, 57.0, 58.7, 60.0, 65.0; *m/z* (EI, 70 eV) 216 (M⁺, 9%), 187 (38), 117 (42). The *exo*-epoxide **15** (51% yield) was obtained in a similar manner utilizing one molar equivalent of MCPBA. δ_H(CDCl₃, 200 MHz) 1.40–1.52 (q, *J* 11, 1H), 1.62–1.83 (m, 3H), 2.52–2.87 (m, 3H), 2.89–3.22 (m, 3H), 3.29–3.44 (m, 4H),

5.48–5.51 (d, *J* 6, 1H), 5.64–5.67 (d, *J* 6, 1H); $\delta_{\text{C}}(\text{CDCl}_3, 50 \text{ MHz}, ^1\text{H-decoupled})$ 35.2, 37.8, 48.2, 49.3, 52.9, 53.6, 54.1, 55.1, 57.4, 58.4, 60.0, 62.7, 129.6, 138.5; *m/z* (EI, 70 eV) 200 (M^+ , 7%), 184 (4), 172 (58), 143 (32), 129 (100). The endo-epoxide **16** was prepared from **8**. The latter (70 mg, 0.25 mmol) was dissolved in THF (10 cm³) at 0 °C, and to the solution was added NaH (12.2 mg, 0.50 mmol) under nitrogen atmosphere. The mixture was stirred for 10 min, then was quenched by the addition of saturated NH₄Cl solution. The organic products were extracted with ether. The ether phase was washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Endo-Epoxide **16** was collected by silica gel chromatograph eluted with CH₂Cl₂:hexane (1:6) to yield a colorless solid (24 mg, 0.12 mmol, yield 47%) (Found M^+ , 200.1201. C₁₄H₁₆O requires *M*, 200.1201); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3022, 2921, 1737, 1456, 1373, 1235, 1019; $\delta_{\text{H}}(\text{CDCl}_3, 200 \text{ MHz})$ 1.70–1.83 (m, 2H), 1.88–1.98 (m, 2H), 2.43–2.90 (m, 4H), 3.15–3.46 (m, 5H), 3.66–3.77 (q, *J* 12, 1H), 5.50–5.55 (d, *J* 6, 1H), 5.70–5.74 (d, *J* 6, 1H); $\delta_{\text{C}}(\text{CDCl}_3, 50 \text{ MHz}, ^1\text{H-decoupled})$ 34.8, 39.7, 47.6, 50.5, 52.0, 53.6, 54.7, 55.3, 60.4, 64.6, 65.2, 68.1, 131.9, 133.5; *m/z* (EI, 70 eV) 200 (M^+ , 5%), 172 (7), 141 (7), 129 (24), 115 (44).

Pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecanediols **17**, **18**, **19**

To a two-necked round bottomed flask (150 cm³) fitted with nitrogen inlet and outlet was added compound **2** (1.27 g, 6.9 mmol) in THF (20 cm³) under nitrogen atmosphere. The solution was stirred by a magnetic bar at room temperature for 10 min, then to it was added a solution of BH₃·THF (1.0 M in THF) (14 cm³, 14 mmol). The reaction was quenched after 24 h by adding distilled water, followed by NaOH (3 M, 10 cm³) and H₂O₂ (35%, 20 cm³). The solution was stirred for another 6 h, then it was poured into saturated aqueous K₂CO₃ in a separation funnel. The resulting mixture was extracted several times with CH₂Cl₂, dried over anhydrous MgSO₄, and concentrated *in vacuo*. Three diols were isolated from the crude product, which was purified by a silica gel column chromatograph eluted with hexane:ethyl acetate (1:4). In addition to the diols **17** (350 mg, 23%), **18** (167 mg, 11%) and **19** (182 mg, 12%), there was also ca. 15% (230 mg) yield of a product hydrolyzed at only one of the two olefinic sites. Physical data for **17**: mp 173–175 °C; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3257, 2918, 1459, 1444, 1349, 1049; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 1.20 (dt, *J* 8, 14, 1H), 1.40 (dm, *J* 14, 1H), 1.69 (m, 3H), 1.80–2.10 (m, 5H), 2.39 (qm, *J* 9, 1H), 2.54–2.65 (m, 2H), 2.65–2.80 (m, 1H), 2.98 (dd, *J* 10, 20, 1H), 3.00–3.18 (m, 1H), 3.34 (dt, *J* 10, 20, 2H), 4.26 (m, 2H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz}, ^1\text{H-decoupled})$ 35.30, 38.13, 39.36, 44.48, 44.86, 45.27, 48.17, 56.29, 57.12, 57.33, 59.23, 60.59, 77.07, 81.59; *m/z* (EI, 70 eV) 220 (M^+ , 25%), 202 ($\text{M}^+ - 18$, 60). Physical data for **18**: mp 178–180 °C (Found *C*, 76.20; *H*, 9.02; M^+ , 220.1469. C₁₄H₂₀O₂ requires *C*, 76.32; *H*, 9.15%; *M*, 220.1463); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3281, 2940, 1455, 1337; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 1.25–1.34 (dt, *J* 7, 14, 2H), 1.82 (dt, *J* 7, 14, 2H), 1.88–2.09 (m, 4H), 2.53–2.69 (m, 7H), 2.90 (q, *J* 10, 1H), 3.29 (qm, *J* 10, 2H), 4.48 (dd, *J* 6, 10, 2H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz}, ^1\text{H-decoupled})$ 40.32, 44.23, 45.26, 48.66, 56.50, 57.70, 60.23, 75.38; *m/z* (EI, 70 eV) 220, (M^+ , 3%), 202 ($\text{M}^+ - 18$, 36), 184 ($\text{M}^+ - 36$, 26). Physical data of **19**: mp 148–149 °C (Found *C*, 76.18; *H*, 9.19; M^+ , 220.1460. C₁₄H₂₀O₂ requires *C*, 76.32; *H*, 9.15%; *M*, 220.1463); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3283, 2939, 1459, 1336; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 1.22–1.31 (dt, *J* 7, 14, 2H), 1.52–1.63 (m, 4H), 1.93–2.05 (m, 4H), 2.30–2.42 (m, 2H), 2.55–2.62 (m, 1H), 2.98–3.04 (m, 3H), 3.36 (dd, *J* 9, 9, 2H), 4.28–4.32 (m, 2H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz}, ^1\text{H-decoupled})$ 36.67, 37.60, 45.65, 47.54, 56.42, 57.12, 59.76, 81.89; *m/z* (EI, 70 eV) 220, (M^+ , 10%), 202 ($\text{M}^+ - 18$, 100), 184 ($\text{M}^+ - 36$, 27), 167 (18), 149 (49).

Pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecanediones **20**, **21**, **22**, **23**

A typical procedure for the oxidations are outlined as follows: to a two-necked round bottomed flask (100 cm³) fitted with

nitrogen inlet and outlet was added compound **17** (350 mg, 1.60 mmol) and pyridinium dichromate (1.50 g, 3.90 mmol) under a nitrogen atmosphere. To the flask was injected through a syringe CH₂Cl₂ (30 cm³) and the solution was stirred for 24 h at room temperature. The solution was diluted with THF (40 cm³) and was filtered. The filtrate was concentrated *in vacuo* and was applied onto a silica gel column chromatograph eluted with hexane:ethyl acetate (1:1). Dione **20** thus collected may be crystallized directly (270 mg, 79%). Physical data for **20**: mp 208–209 °C (Found *C*, 77.76; *H*, 7.33. C₁₄H₁₆O₂ requires *C*, 77.74; *H*, 7.46%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2944, 1729, 1719; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.50 (ddd, *J* 11 ~ 12, 1H), 1.90–2.00 (dt, *J* 7, 14, 1H), 2.05–2.10 (m, 2H), 2.22 (d, *J* 18, 1H), 2.45–2.60 (m, 3H), 2.60–2.80 (m, 3H), 3.10–3.45 (m, 4H), 3.56 (q, *J* 10, 1H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz}, ^1\text{H-decoupled})$ 37.94, 39.57, 40.49, 40.73, 41.82, 47.58, 47.65, 53.58, 54.43, 56.17, 58.53, 59.42, 221.95, 223.72; *m/z* (EI, 70 eV) 216 (M^+ , 100%), 198 ($\text{M}^+ - 18$, 30), 188 ($\text{M}^+ - 28$, 20). Physical data for **21**: mp 205–206 °C (Found *C*, 77.75; *H*, 7.33. C₁₄H₁₆O₂ requires *C*, 77.74%; *H*, 7.46%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2945, 1731, 1448, 1401, 1317; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 1.34–1.43 (dt, *J* 7, 14, 2H), 2.12–2.23 (m, 2H), 2.33 (d, *J* 19, 2H), 2.58 (m, 1H), 2.61 (d, *J* 19, 2H), 2.80–2.87 (m, 2H), 3.05–3.15 (m, 2H), 3.31 (q, *J* 8, 1H), 3.37 (qm, *J* 9, 2H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz}, ^1\text{H-decoupled})$ 39.16, 40.95, 46.98, 47.34, 55.59, 57.76, 59.98, 219.55; *m/z* (EI, 70 eV) 216, (M^+ , 100%), 198 ($\text{M}^+ - 18$, 20), 188 ($\text{M}^+ - 28$, 30). NMR data for **22**: $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz}, ^1\text{H-decoupled})$ 36.77, 41.76, 42.80, 49.00, 54.27, 54.98, 59.95, 223.22. Physical data for **23** (mixed with minor amount of **22**): mp 203–215 °C (lit.⁵ 210–226 °C) (Found: *C*, 77.47; *H*, 7.47. C₁₄H₁₆O₂ requires *C*, 77.74; *H*, 7.46%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3410, 2946, 1721; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 1.40 (dm, *J* 16, 1H), 1.90–2.10 (m, 5 H), 2.37 (d, *J* 13, 1H), 2.51 (t, *J* 10, 1H), 2.75–2.85 (m, 3H), 2.85–2.90 (m, 1H), 2.90–3.05 (m, 2H), 3.05–3.15 (m, 2H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz}, ^1\text{H-decoupled})$ 32.83, 44.83, 48.52, 48.74 (2C), 52.04, 52.73, 53.30, 54.28, 56.69, 58.08, 59.39, 87.52, 227.81; *m/z* (EI, 70 eV) 216, (M^+ , 100%), 198 ($\text{M}^+ - 18$, 75), 188 ($\text{M}^+ - 28$, 40).

2-Oxahexacyclo[7.5.1.0^{3,13}.0^{5,12}.0^{7,11}.0^{10,14}]pentadecan-3-ol **26**

To a solution of **21** (0.22 g, 1.00 mmol) in methanol (30 cm³) was added NaBH₄ (40 mg, 1.00 mmol) at 0 °C. The reaction mixture was stirred for 1 h, then was quenched by the addition of saturated aqueous NH₄Cl (30 cm³). The resulting mixture was extracted with ether (30 cm³ × 5), washed with brine, dried over anhydrous MgSO₄, and concentrated *in vacuo*. Compound **26** (0.19 g, 0.86 mmol, 85% yield) was purified by column chromatography as a colorless oil (Found M^+ , 218.1311. C₁₄H₁₈O requires *M*, 218.1307); $\nu_{\text{max}}(\text{CDCl}_3)/\text{cm}^{-1}$ 3500–3300, 2970, 1070; $\delta_{\text{H}}(\text{CDCl}_3, 200 \text{ MHz})$ 1.92–2.17 (m, 8H), 2.50–2.60 (m, 1H), 2.69–2.75 (m, 2H), 3.00–3.40 (m, 5H), 4.82 (dd, *J* 3.6, 3.6, 1H); $\delta_{\text{C}}(\text{CDCl}_3, 50 \text{ MHz}, ^1\text{H-decoupled})$ 42.03, 42.34, 43.17, 45.59, 46.47, 47.26, 47.77, 60.49, 60.91, 62.25, 62.80, 65.19, 90.81, 120.22; *m/z* (EI, 50 eV) 218 (M^+ , 5%), 201 (100).

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