Diels−Alder Cycloaddition of 11-Oxapentacyclo[6.5.2.2^{3,6}.0^{2,7}.0^{9,13}]-heptadeca-4,14,16-triene-4,5-dicarboxylic Anhydride with Cyclopentadiene and the Transannular Reactions of the Resulting Cycloadducts

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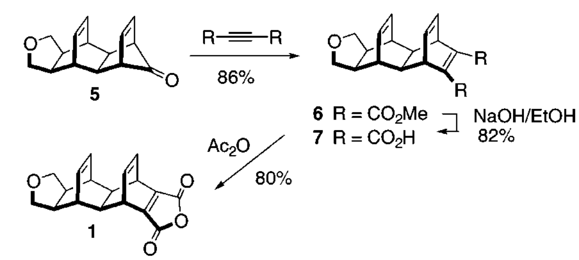
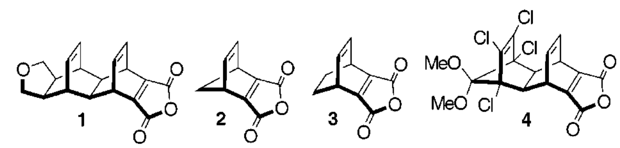
Rigid polycyclic molecules having isolated double bonds located in the laticyclic topology[1] and spatially in close proximity have provided suitable frameworks for study of transannular reactions[2] and orbital interactions.[3] In the aspect of chemical reactions, face-proximate double bonds in these systems can undergo facile photochemical [2 + 2] cycloaddition to produce cyclobutane rings (closure, O-type), and stepwise electrophilic additions leading to the transannular bridge formation in either a cross (N-type) or a parallel (U-type) manner.[4] As our interest in the synthesis and transannular reactions of polycyclic hydrocarbons continues, we recently have undertaken the preparation of the title compound **1**, to be used as a dienophile in the Diels−Alder cycloadditions with cyclic dienes, for the construction of polycyclic compounds containing three laticyclic conjugated, face-to-face double bonds.

Compound **1** has nonequivalent π-faces about the anhydride double bond and is expected to display facial selectivity in the Diels−Alder cycloaddition. We anticipated that the Diels−Alder cycloaddition would likely proceed via syn-side (relative to the etheno bridge in **1**) attack of the diene upon **1**. This expectation is contrary to the behavior of bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride (**2**), which is known to undergo the Diels−Alder cycloadditions with dienes exclusively on the face anti to the etheno bridge of **2**.[5] However, the cycloaddition of cyclopentadiene onto bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylic anhydride (**3**) takes place preferentially at its syn face.[6] In the Diels−Alder cycloadditions of the more elaborated analogous anhydride **4** with cyclic dienes, exclusive syn-facial selectivity was observed.[7] The syn-facial selectivity was again found in the Diels−Alder cycloaddition of anhydride **1** with cyclopentadiene. The reaction proceeded with the attack of diene upon the activated double bond of **1** via the face syn to the etheno bridge exclusively, thereby affording only two of the four possible cycloadducts. In this paper, we wish to report the structures and the transannular reactions of the resulting Diels−Alder cycloadducts.

Scheme 1





Results and Discussion

The preparation of maleic anhydride **1** was carried out by reactions shown in the Scheme 1, starting from the pentacyclic dienone **5** following the established procedure with modification. Dienone **5** could be easily obtained from the Diels−Alder cycloadduct of 1,1-dimethoxy-2,3,4,5-tetrachlorocyclopentadiene and *p*-benzoquinone in several steps.[8−10] Thus, when a solution of dienone **5** and dimethyl acetylenedicarboxylate in toluene was heated at 100 °C, decarbonylation of **5** occurred followed by the Diels−Alder cycloaddition to produce adduct **6** in 86% yield. The cycloaddition proceeded with dienophile approaching the resulted 1,3-cyclohexadiene substructure from the less hindered exo face to yield **6** exclusively. Intramolecular dehydration of dicarboxylic acid **7**, obtained from hydrolysis of adduct **6**, by heating with acetic anhydride gave the desired maleic anhydride **1** in 56% overall yield from **5**. The formation of anhydride ring moiety is confirmed by the presence of two characteristic absorption bands at 1836 and 1766 cm^{-1} in the infrared spectrum of **1**. The presence of two parallel face-to-face etheno bridges in **1** and, hence the course of forming adduct **6** in the Diels−Alder cycloaddition, was suggested by two doublet-of-doublets signals at δ 6.01 and 5.85 in

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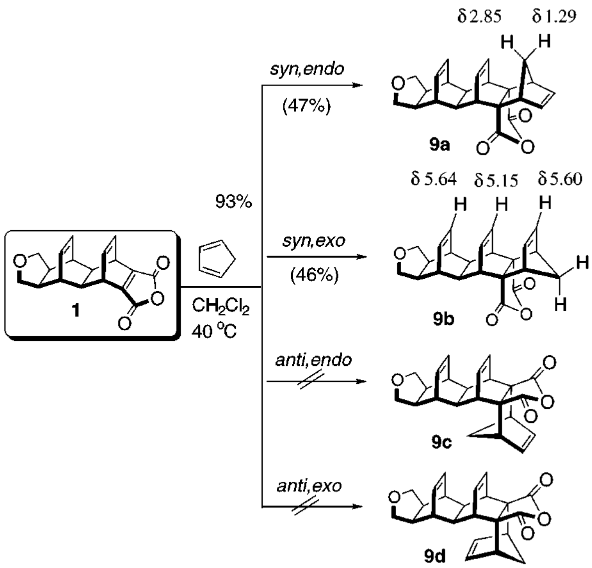
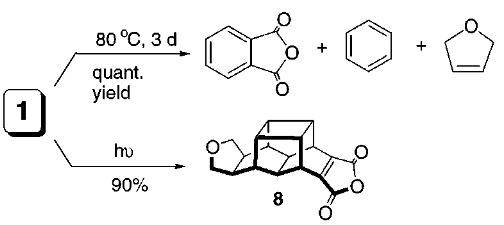
Scheme 2



the ¹H NMR spectrum that are ascribed to the vinyl hydrogens of two mutually shielded double bonds of bicyclo[2.2.2]octenyl substructures in **1**[11] and further confirmed by the intramolecular [2 + 2] photocyclization to give the cage compound **8** (eq 1). Anhydride **1** is

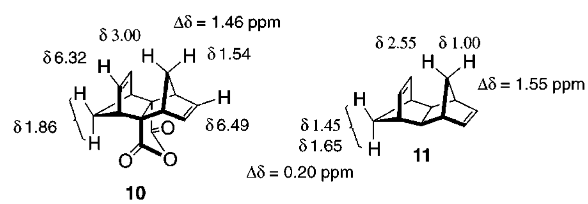


(1)

thermally unstable and on heating at 80 °C for 3 days decomposes quantitatively to phthalic anhydride, 2,5-dihydrofuran, and benzene (eq 1). Therefore, the Diels−Alder cycloaddition of **1** was performed at 40 °C in dichloromethane.

Diels−Alder Cycloaddition with Cyclopentadiene. The electronically activated double bond presented in maleic anhydride **1** readily undergoes the Diels−Alder cycloaddition with cyclopentadiene. Thus, when a solution of anhydride **1** and cyclopentadiene (10 equiv) in dichloromethane was heated at 40 °C in a vacuum-sealed glass tube, the reaction produced only two of four possible stereoisomeric cycloadducts (syn,endo, syn,exo, anti,endo, and anti,exo adducts, Scheme 2)[12] ın a ratio of 1:1, as determined by ¹H NMR spectral analysis of the crude product mixture immediately after workup procedure without further separation and purification. These two adducts were separated by column chromatography and purified by recrystallization from CH_2Cl_2−hexane to give adducts **9a** and **9b** in a total of 93% yield (Scheme 2). Elemental and mass spectral analyses established the cycloadducts to be of 1:1 nature and isomeric. Both adducts have inherent C_s symmetry as is evident from their rather simple ¹H and ¹³C NMR spectra,which are consistent with the structural assignments.

The ¹H NMR spectrum of adduct **9a** exhibits absorption signals for vinyl hydrogens at δ 6.37, 5.80, and 5.76, the former being like that in *exo*-bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic anhdride (**10**)[5] and the later two signals ascribed to the two parallel aligned, mutually shielded double bonds,[11] comparable to those in **1**. A diagnostic feature that led us to assign stereostructure **9a** for this adduct is the unusual absorption of an AB pattern (J = 9.6 Hz) generated by the two hydrogens on the methano bridge at δ 2.85 and 1.29 with a large difference in chemical shifts ($\Delta\delta$ = 1.56 ppm) and an unusual downfield absorption for one of these two hydrogens. This kind of absorption pattern is well-documented in the literature concerning the ¹H NMR spectra of fused norbornyl systems.[13] For example, the relative absorption positions of the hydrogens at two environmentally different methano bridges of anhydride **10**[5] and the parent hydrocarbon, the dechlorinated aldrin **11**[14] are demonstrative for our stereochemical determination of adduct **9a**. For compound **10**, a separation of $\Delta\delta$ = 1.46 ppm is observed for the two geminal hydrogens that are on the bridge proximal to the $\Delta^{2,3}$ double bond. Similar behavior is observed for the corresponding protons in **11** with a separation of $\Delta\delta$ = 1.55 ppm. Due to the steric compression against the π cloud of the double bond,[15] the hydrogen directly facing the $\Delta^{2,3}$ double bond in **10** and **11** experiences very strong deshielding effect and thus displays a large downfield shift to appear at δ 3.00 and 2.55, respectively. The other pair of bridge hydrogens in **10** and **11** behaves rather normally, comparable to that of norbornene (at δ 1.08 and 1.33; $\Delta\delta$ = 0.25 ppm),[16] with values of less than $\Delta\delta$ = 0.20 ppm for the separation of these two hydrogens. The assignment of stereostructure of **9a** based upon these special features in the ¹H NMR spectrum is confirmed by an X-ray single-crystal structure of **9a** (Figure 1a).[17]



On the other hand, in the ¹H NMR spectrum of adduct **9b**, the geminal hydrogens on the methano bridge appear normally at δ 1.28 and 1.43 with J = 10.2 Hz and $\Delta\delta$ = 0.15 ppm, comparable to those in norbornene, **10**, and **11**. The absorption signals for three groups of vinyl hydrogens in **9b** appear at δ 5.64 (dd, J_1 = 3.3, J_2 = 4.5 Hz), δ 5.60 (m), and δ 5.15 (dd, J_1 = 3.3, J_2 = 4.8 Hz), which suggests the vinyl hydrogens are on mutually shielded double bonds and those of central double bond

(11) This consequence is typical for *endo,endo*-dimethanonaphthalene and other related homologous systems. Astin, K. B.; Mackenzie, K. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1004.

(12) Syn and anti refer to the relative side of the attachment of diene and the existing etheno bridge in **1** and endo and exo refer to the orientation of the anhydride moiety relative to the newly formed bicyclic ring nucleus in accordance to the Alder endo rule.

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(16) Tori, K.; Takano, Y.; Kitahonoki, K. *Chem. Ber.* **1964**, *97*, 2798.

(17) The authors have deposited X-ray data with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

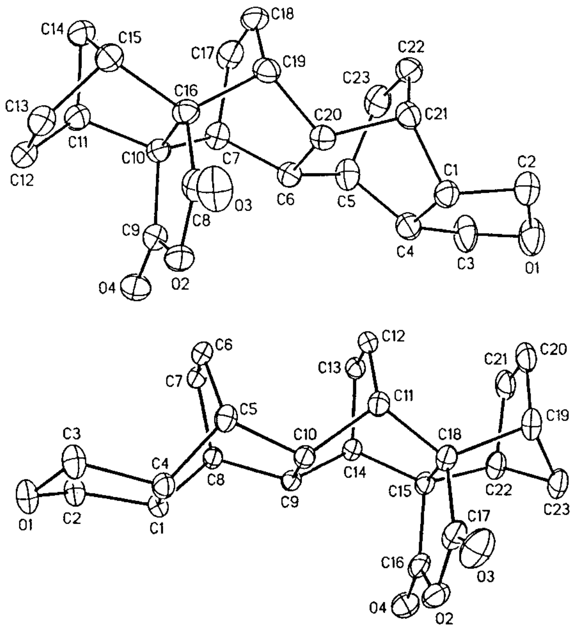
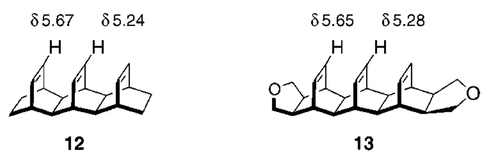
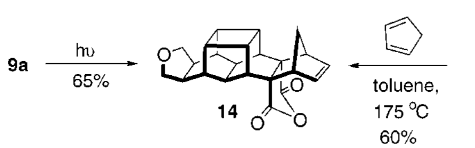


Figure 1. ORTEP drawings of compounds **9a**,**b**.

(at δ 5.15) are shielded by two flanking double bonds. Groups of vinyl hydrogens displaying comparable chemical shifts have been noted in the laticyclic conjugated trienes **12**[18] and **13**.[10] These shifts support our structural assignment of syn,exo adduct **9b** as having three double bonds aligned in parallel and located face-to-face in proximity. An X-ray structural analysis (Figure 1b) unequivocally established the stereostructure of **9b**.[17] The establishment of the stereostructures of both adducts **9a** and **9b** suggests that the cycloaddition of cyclopentadiene to maleic anhydride **1** takes place exclusively on the syn face of **1**, but without stereochemical discrimination between the endo and exo approaches.



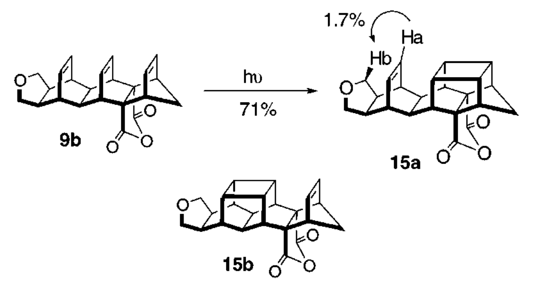
Transannular Reactions. As expected, when a solution of syn,endo adduct **9a** in benzene–acetone (10:1) was irradiated with a medium-pressure Hg lamp for 8 h, the reaction produced the cage compound **14** in 65% isolated yield after chromatography on silica gel (eq 2). In addition



(2)

to an absorption of AB pattern generated by the geminal hydrogens on the methano bridge, centered at δ 1.68 with $J = 9.6$ Hz and $\Delta\delta = 0.29$ ppm, the ^{1}H NMR spectrum of **14** displays a dd at $\Delta\delta$ 6.38 for the vinyl hydrogens in the bicyclo[2.2.1]heptene substructure. A cage compound identical to the photoadduct **14** could also be obtained from the Diels–Alder cycloaddition of the cage compound **8** with cyclopentadiene (eq 2). Due to the low reactivity of **8**, the cycloaddition had to be carried out in toluene at 175 °C. It was found that cyclopentadiene approached **8** exclusively from the face syn to the cyclobutane ring and followed Alder's endo rule to give **14**.

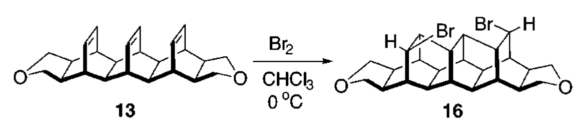
The syn,exo adduct **9b** has three parallel, face-to-face aligned double bonds. In principle, intramolecular [2 + 2] photocyclization of **9b** could conceivably deliver two photoadducts, **15a** and **15b**. Experimentally, irradiation of a solution of **9b** in benzene–acetone (10:1) was found to result in virtually complete formation of the photoadduct **15a** via addition of the norbornenyl double bond to the central double bond (eq 3). The structural assignment



(3)

of photoadduct **15a** is supported by the ^{1}H NMR, ^{13}C NMR, and NOE spectral analyses. In addition to the enhancement of signals at δ 2.44 due to hydrogens including those of cyclobutane ring, an enhancement (1.7%) of absorption signal (at δ 3.34) ascribed to the "inside" methylene hydrogens of the tetrahydrofuran ring is clearly observed when the vinyl hydrogens of the etheno bridge in **15a** (at δ 6.07) are irradiated. The regioselectivity leading to the formation of photoadduct **15a**, but not **15b**, must be determined by the combination of factors: (1) the norbornenyl double bond is more strained and more reactive toward addition reactions than the bicyclo[2.2.2]octenyl double bond,[19] and (2) the distance between two bicyclo[2.2.2]octenyl double bonds (2.988 Å) is longer than the distance between the norbornenyl double bond and the central double by 0.099 Å.[3c]

Recently, we have investigated the bromination of polycyclic olefin **13**, which contains three face-to-face double bonds aligned in parallel and in close proximity. The addition occurred transannularly, resulting in the sequential construction of bridges across the double bonds in a cross (N-type)[4] manner to form dibromide **16** (eq 4).[10]



(4)

In contrast, the electrophilic addition of triene **9b** in $CHCl_3$ with bromine furnished dibromide **17** as the only product (Scheme 3). The ^{1}H NMR and ^{13}C NMR spectra of dibromide **17** are complex, indicating the lack of any symmetry element in the molecule. The structure and stereochemistry of **17** was thus unequivocally established by single-crystal X-ray diffraction analysis.[17] The ORTEP drawing of structure **17** is shown in Figure 2, which shows that two bromine atoms are located to have endo,exo sterochemistry (or anti and syn with respect to

(18) (a) Grimme, W.; Pohl, K.; Wortmann, J.; Frowein, D. *Liebigs Ann.* **1996**, 1905–1916. (b) Grimme, W.; Wortmann, J.; Frowein, D.; Lex, J.; Chen, G.; Gleiter, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1893.

(19) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *J. Am. Chem. Soc.* **1980**, *102*, 3951.

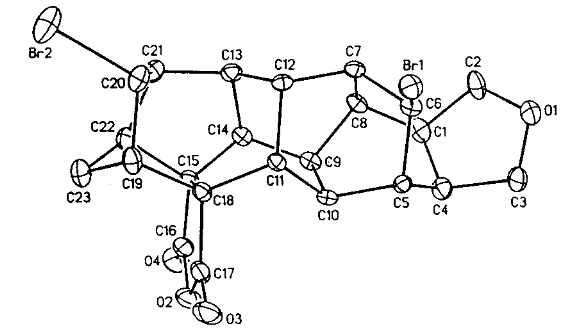
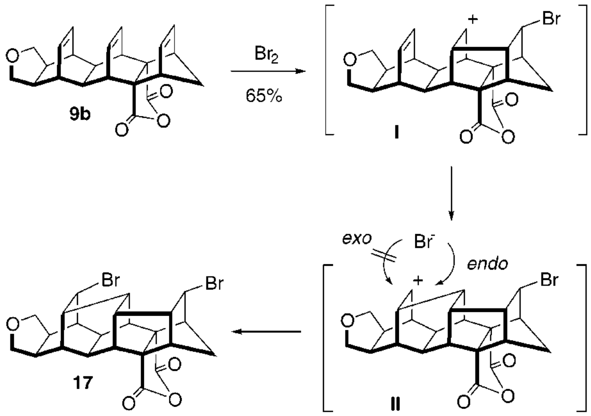


Figure 2. ORTEP drawing of compound **17**.

Scheme 3



tetrahydrofuran ring and methano bridge, respectively). The mechanism that accounts for the formation of dibromide **17** from the bromination of triene **9b** is outlined in Scheme 3. Bromination occurred initially at the sterically less hindered exo side of the norbornene substructure, subsequently followed by transannular formation of the carbon−carbon bridge in the parallel (U-type) manner to give intermediate carbocation **I**. The second transannular bridge formation in **I** occurred in the cross (N-type) manner leading to cation **II**, which was then captured by bromide ion approaching from the sterically less hindered "endo-side" to give dibromide **17**. It is interesting to note that the mode of the first transannular bridge formation (parallel, U-type) is in line with the transannular additions of analogous systems involving norbornene moiety[20] and the second (**I** → **II**) parallels the bromination reactions of triene **13** (cross, N-type) shown by eq 4 and other systems having an *endo,endo*-diethenonaphthalene skeleton.[4,21]

Experimental Section

General Methods. Melting points were determined in open capillaries and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on E. Merck silica gel $60F_{254}$ plate (0.25 mm). Flash chromatography was performed on E. Merck silica gel (230−400 mesh). ^{1}H NMR spectra were measured at 300 MHz and ^{13}C NMR at 75.4 MHz, respectively. Chemical shifts are referenced to TMS or to the residual H in perdeuterated solvents (7.26 ppm for $CDCl_3$). ^{13}C NMR multiplicities were determined using DEPT pulse sequences. 2D COSY(homo and hetero) experiments were performed with compounds **9a**, and MS spectra were determined at 70 eV in the EI mode unless otherwise stated. IR spectra in KBr were determined by FT-IR. Microanalyses were performed by Analytical Centers of National Cheng Kung and Taiwan Universities, Taiwan.

(1α,2β,3α,6α,7β,8α,9α,13α)-Dimethyl 11-Oxapentacyclo[6.5.2.2^{3,6}.0^{2,7}.0^{9,13}]heptadeca-4,14,16-triene-4,5-dicarboxylate (6). A solution of the dienone **5** (0.14 g, 0.61 mmol) and dimethyl acetylenedicarboxylate (0.11 g, 0.77 mmol) in toluene (15 mL) was stirred in a vacuum-sealed glass tube at 100 °C for 48 h. The mixture was concentrated to give the crude dicarboxylate **6**. Recrystallization from diethyl ether afforded the pure **6** (0.18 g, 86%) as a white solid: mp 135−136 °C; R_f 0.13 (2:1 hexane/EtOAc); IR (KBr) 1712, 1638, 711 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.12 (s, 2H), 2.41 (m, 2H), 2.47 (m, 2H), 3.24 (dd, 2H, J = 5.4, 8.6 Hz), 3.67−3.72 (m, 4H), 3.70 (s, 6H), 5.69 (dd, 2H, J = 3.3, 4.5 Hz), 5.90 (dd, 2H, J = 3.3, 4.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.73 (d), 42.77 (d), 44.11 (d), 47.51 (d), 52.10 (q), 71.79 (t), 131.49(d), 132.29 (d), 144.93 (s), 166.54 (s); MS (EI, 70 eV) m/z (relative intensity) 342 (M$^+$, 15), 163 (100); HRMS m/z calcd for $C_{20}H_{22}O_5$ 342.1467, obsd 342.1459. Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.17; H, 6.55.

(1α,2β,3α,6α,7β,8α,9α,13α)-11-Oxapentacyclo[6.5.2.2^{3,6}.0^{2,7}.0^{9,13}]heptadeca-4,14,16-triene-4,5-dicarboxylic Acid (7). To a solution of dicarboxylate **6** (2.00 g, 5.85 mmol) in ethanol (25 mL) was added dropwise aqueous NaOH (9.6 M, 70 mL) at 0 °C. The resulting solution was heated under reflux for 4 h and then cooled to room temperature. The solvent was concentrated to half of the volume in vacuo and then acidified with HCl until precipitation occurred. The mixture was extracted with EtOAc (100 mL × 3), and the organic layers were washed with water (30 mL). After the mixture was dried over $MgSO_4$, the solvent was evaporated in vacuo, and the residue was purified by recrystallization from EtOAc/hexane to give **7** (1.50 g, 82%) as a white solid: mp 154 °C (dec, hexane/acetonitrile); R_f 0.22 (8:1 EtOAc/MeOH); IR (KBr) 3430, 1718 cm^{-1}; ^{1}H NMR (CD_3OD, 300 MHz) δ 2.16 (s, 2H), 2.55 (m, 4H), 3.30−3.34 (m, 2H), 3.74 (m, 2H), 3.95 (m, 2H), 4.97 (s, 2H), 5.75 (m, 2H), 5.96 (dd, 2H, J = 3.3, 4.5 Hz); ^{13}C NMR (CD_3OD, 75 MHz) δ 39.15 (d), 43.97 (d), 46.18 (d), 48.85 (d), 72.88 (t), 132.78 (d), 133.53 (d), 147.83 (s), 169.51 (s); MS (FAB) m/z (relative intensity) 315 (MH$^+$, 50), 154 (100); HRMS (FAB) m/z calcd for $C_{18}H_{19}O_5$ (M$^+$ + H) 315.1233, obsd 315.1245. Anal. Calcd for $C_{18}H_{19}O_5$: C, 68.78; H, 5.78. Found: C, 68.56; H, 5.82.

(1α,2β,3α,6α,7β,8α,9α,13α)-11-Oxapentacyclo[6.5.2.2^{3,6}.0^{2,7}.0^{9,13}]heptadeca-4,14,16-triene-4,5-dicarboxylic Anhydride (1). A solution of dicarboxylic acid **7** (3.90 g, 12.4 mmol) in acetic anhydride (17.70 g, 0.17 mmol) was heated to 60 °C for 1 h. The resulting solution was cooled to room temperature, and the precipitate was collected by filtration and washed with diethyl ether (100 mL) to afford carboxylic anhydride **1** (2.93 g, 80%) as a white solid. Repeated recrystallization from acetonitrile−hexane gave an analytical sample: mp 120−122 °C; R_f 0.22 (8:1 EtOAc/MeOH); IR (KBr) 1836, 1766 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.13 (s, 2H), 2.47 (m, 2H), 2.62 (m, 2H), 3.34 (dd, 2H, J = 5.1, 8.7 Hz), 3.77 (m, 2H), 3.93 (m, 2H), 5.85 (dd, 2H, J = 3.3, 4.5 Hz), 6.01 (dd, 2H, J = 3.3, 4.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.72 (d), 39.71 (d), 43.52 (d), 47.57 (d), 71.70 (t), 131.47 (d), 131.94 (d), 156.68 (s), 160.80 (s); MS (El, 70 eV) m/z (relative intensity) 296 (M$^+$, 21), 78 (100); HRMS m/z calcd for $C_{18}H_{16}O_4$ (M$^+$) 296.1049, obsd 296.1045. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.01; H, 5.50.

Photochemical Reaction of 1. Formation of (1α,2β,3β,4α,7α,11α,12α,16α)-14-Oxaheptacyclo[8.6.1.0^{2,7}.0^{4,9}.0^{8,17}.0^{10,17}.0^{12,16}]heptadeca-5,6-dicarboxylic Anhydride (8). A solution of anhydride **1** (0.24 g, 0.81 mmol) in benzene−acetone (25 mL, 10:1) was irradiated through Pyrex at 10−15 °C with a 450 W medium-pressure mercury lamp (Hanovia) in a water immersion well apparatus. During the irradiation, a stream of nitrogen was passed through the solution. After 8 h of irradiation, the solvent was evaporated and the residue was purified by chromatography on silica gel (EtOAc−hexane 1: 24) to give **8** (0.21 g, 90%): mp >260 °C (dec after recrystallization from CH_2Cl_2/hexane), R_f 0.22 (EtOAc/MeOH 8:1); IR (KBr) 1834, 1767 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.88 (d, 2H, J = 1.5 Hz), 2.02 (dd, 2H, J = 0.9, 1.8 Hz), 2.49−2.55 (m, 4H), 2.86 (m, 2H), 3.14 (m, 2H), 3.72 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 33.82 (d), 35.27 (d), 37.68 (d), 37.99 (d), 42.93 (d), 43.47 (d), 73.16 (t), 149.36 (s), 162.59 (s); MS(FAB)

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m/z (relative intensity) 297 (MH$^+$, 24), 154 (100); HRMS (FAB) *m/z* calcd for $C_{18}H_{17}O_4$ (M$^+$ + H): 297.1127, obsd 297.1111. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.86; H, 5.31.

Cycloaddition of 1 with 1,3-Cyclopentadiene. Formation of (1α,2β,3α,4β,8β,9α,10β,11α,12β,13α,16α,17β)-6-Oxaheptacyclo[9.6.2.2^{3,9}.1^{13,16}.0^{2,10}.0^{4,8}.0^{12,17}]docosan-14,18,20-triene-12,17-dicarboxylic Anhydride (9a) and Isomeric Anhydride 9b. A solution of carboxylic anhydride **1** (0.50 g, 1.69 mmol) and 1,3-cyclopentadiene (1.11 g, 16.9 mmol) in dry CH_2Cl_2 (2 mL) was stirred in a vacuum-sealed glass tube at 40 °C for 20 d. The solution was concentrated and chromatographed through a silica gel column with EtOAc/hexane (1: 6) as eluent to afford cycloadducts **9a** (0.29 g, 47%) and **9b** (0.28 g, 46%). The analytical samples of **9a** and **9b** were obtained from further recrystallization in CH_2Cl_2−hexane.

9a: mp 225 °C dec; R_f 0.36 (2:1 hexane/EtOAc); IR (KBr) 1850, 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (dm, 1H, *J* = 9.6 Hz), 2.17 (d, 2H, *J* = 0.6 Hz), 2.44 (m, 2H), 2.51 (m, 2H), 2.84 (dm, 1H, *J* = 9.6 Hz), 2.98 (m, 2H), 3.12 (m, 2H), 3.26 (dd, 2H, *J* = 2.7, 9.9 Hz), 3.72 (m, 2H), 5.76 (dd, 2 H, *J* = 3.3, 4.5 Hz), 5.80 (dd, 2 H, *J* = 3.0, 4.8 Hz), 6.37 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.86 (d), 40.02 (d), 40.53 (d), 47.00 (d), 49.75 (t), 50.06 (d), 64.21 (s), 71.91 (t), 131.17 (d), 132.27 (d), 140.23 (d), 174.98 (s); MS (El, 70 eV) *m/z* (relative intensity) 362 (M$^+$, 1), 66 (100); HRMS *m/z* calcd for $C_{23}H_{22}O_4$ (M$^+$) 362.1519, obsd 362.1521. Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.20; H, 6.09. **9b**: mp 230 °C dec; R_f 0.43 (2:1 hexane/EtOAc); IR (KBr) 1853, 1768 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (dm, 1H, *J* = 10.2 Hz), 1.43 (dm, 1H, *J* = 10.2 Hz), 2.13 (s, 2H), 2.42 (m, 4H), 2.96 (dd, 2H, *J* = 3.9, 3.9 Hz), 3.08 (m, 2H), 3.23 (dd, 2H, *J* = 5.1, 8.7 Hz), 3.69 (dd, 2H, *J* = 7.2, 7.2 Hz), 5.15 (dd, 2H, *J* = 3.3, 4.8 Hz), 5.60 (m, 2H), 5.64 (dd, 2H, *J* = 3.3, 4.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.81 (d), 39.85 (d), 41.40 (d), 46.96 (d), 47.96 (t), 50.82 (d), 62.24 (s), 71.87 (t), 129.36 (d), 132.36 (d), 136.60 (d), 177.14 (s); MS (El, 70 eV) *m/z* (relative intensity) 362 (M$^+$, 14), 92 (100); HRMS *m/z* calcd for $C_{23}H_{22}O_4$ (M$^+$) 362.1519, obsd 362.1514.

Photochemical Reaction of 9b. Formation of (1α,2β,3β,4α,6α,9α,10α,11β,12α,13β,17β,18α,19β)-15-Oxanonacyclo[10.7.1.2^{12,18}.0^{2,6}.0^{3,10}.0^{4,8}.0^{7,20}.0^{11,19}.0^{13,17}]-21-docosen-2,3-dicarboxylic Anhydride (15a). Triene **9b** (0.14 g, 0.39 mmol) in benzene−acetone (25 mL, 10:1) was irradiated using the procedure described for the photochemical reaction of **1** to give **15a** (0.99 g, 71%): mp 243−244.5 °C (hexane/chloroform); R_f 0.43 (2:1 hexane/EtOAc); IR (KBr) 1859, 1777 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.37 (ddd, 1H, *J* = 1.5, 1.5, 11.7 Hz), 1.66 (dm,1H, *J* = 11.7 Hz), 1.87 (s, 2H), 2.27 (d, 2H, *J* = 1.5 Hz), 2.44 (m, 6H), 2.68 (m, 2H), 2.83 (m, 2H), 3.34 (dd, 2H, *J* = 5.1, 8.6 Hz), 3.77−3.82 (m, 2H), 6.07 (dd, 2H, *J* = 3.3, 4.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.64 (t), 34.68 (d), 35.79 (d), 37.77 (d), 42.12 (d), 42.55 (d), 45.98 (d), 49.43 (d), 62.11 (s), 72.35 (t), 130.95 (d), 174.38 (s); MS (El, 70 eV) *m/z* (relative intensity) 362 (M$^+$, 25), 292 (100); HRMS *m/z* calcd for $C_{23}H_{22}O_4$ (M$^+$) 362.1519, obsd 362.1512. Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.35; H, 6.13.

Photochemical Reaction of 9a To Afford 14. Triene **9a** (0.10 g, 0.28 mmol) was irradiated using the procedure described for the photochemical reaction of **1**. Flash column chromatography on silica gel (4% EtOAC/hexane) of the residue obtained on vacuum evaporation of solvent gave **14** (0.65 g, 65%) as a white solid: mp 148 °C (dec, after recrystallization from EtOAc/hexane); R_f 0.36 (2:1 hexane/EtOAc); IR (KBr) 1856, 1776 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.54 (dm, 1H, *J* = 9.6 Hz), 1.61 (m, 2H), 1.83 (dm, 1H, *J* = 9.6 Hz), 2.13 (dd, 4H, *J* = 1.2, 4.8 Hz), 2.47 (dd, 2H, *J* = 2.7, 5.3 Hz), 2.72 (m, 4H), 3.06 (dd, 2H, *J* = 1.2, 3.3 Hz), 3.66 (m, 4H), 6.38 (dd, 2H, *J* = 2.1, 2.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.14 (d), 34.67 (d), 36.33 (d), 37.43 (d), 38.61 (d), 39.78 (d), 48.42 (t), 49.07 (d), 54.58 (s), 73.15 (t), 138.35 (d), 175.27 (s); MS (EI, 70 eV) *m/z* (relative intensity) 362 (M$^+$, 2), 297 (100); HRMS *m/z* calcd for $C_{23}H_{22}O_4$ (M$^+$) 362.1518, obsd 362.1519. Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22;, H, 6.12. Found: C, 76.23; H, 6.07.

Diels−Alder Reaction of Anhydride 8 with Cyclopentadiene To Afford 14. A solution of anhydride **8** (0.15 g, 0.50 mmol) and cyclopentadiene (0.10 g, 1.51 mmol) in toluene (3 mL) was sealed in an autoclave and heated at 175 °C for 10 d. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column with 4% of EtOAc in hexane as eluent to afford cycloadduct **14** (0.18 g, 60%).

Bromination of 9b To Afford Dibromide 17. To a solution containing triene **9b** (0.13 g, 35.8 mmol) in chloroform (5 mL) cooled at 0 °C was added dropwise bromine (0.057 g, 36.0 mmol). The resulting orange solution was stirred for 7 h. Removal of the solvent under reduced pressure left a pale yellow solid that was chromatographed on silica gel with EtOAc/hexane (1:5) as eluent to give **17** (0.12 g, 65%) as a white solid: mp 238−241 °C (hexane/CH_2Cl_2); R_f 0.41(2:1 hexane/EtOAc); IR (KBr) 1862, 1779 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.56−1.69 (m, 3H), 1.92 (dd, 1H, *J* = 3.9, 6.6 Hz), 2.22−2.37 (m, 3H), 2.45−2.57 (m, 4H), 2.70 (dd, 1H, *J* = 6.3, 6.3 Hz), 2.88−2.95 (m, 2H), 3.00 (d, 1H, *J* = 5.4 Hz), 3.18 (d, 1H, *J* = 6.6 Hz), 3.69 (dd, 1H, *J* = 6.0, 9.5 Hz), 3.86−3.93 (m, 3H), 4.82 (dd, 1H, *J* = 1.5, 1.5 Hz), 5.08 (d, 1H, *J* = 5.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.45 (d), 32.65 (d), 34.14 (d), 34.56 (t), 34.87 (d), 35.22 (d), 36.74 (d), 41.11 (d), 41.46 (d), 41.61 (d), 42.37 (d), 42.83 (d), 49.59 (d), 49.67 (d), 50.5 (d), 51.84 (d), 52.27 (d), 58.46 (s) x 2, 70.16 (t), 72.22 (t), 173.19 (s), 173.59 (s); MS (EI, 70 eV) *m/z* (relative intensity) 522 (M$^+$ + 2, 10), 443 (100); HRMS *m/z* calcd for $C_{23}H_{22}O_4Br_2$ (M$^+$) 519.9885, obsd 519.9879. Anal. Calcd for $C_{23}H_{22}O_4Br_2$: C, 52.90; H, 4.25. Found: C, 52.91; H, 4.21.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds; complete X-ray data for **9a**,**b** and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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