Synthesis and Structure Analysis of a Linear Benzannulated Cis-Cisoid-Cis Tetraquinane

Rolf Aebi, Wolfgang Luef, and Reinhart Keese*

Institut für Organische Chemie, Universität of Bern, CH-3012 Bern, Switzerland

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Contrary to expectations, the photoreaction of the benzannulated bicyclo[3.3.0]octene **9** with 2-cyclohexene-1,4-dione (**12**) leads to a [2 + 2] cycloaddition preferentially on the endo- rather than on the exo-side. Upon treatment with trimethylsilyl iodide, the major compound **14** rearranges to **16** with a cis-cisoid-cis triquinane structure. The X-ray structure analysis of **16** revealed a "closed" U-type geometry. The fact that **16** shows different conformations in solution and the solid state is interpreted in terms of a partial pseudorotation of the central cyclopentane ring. According to MM2 calculations, the barrier between the U-shaped and the "opened" conformation is about 10–12 kJ/mol.

Introduction

The synthesis and study of the chemistry of polyquinanes has been an area of wide interest in recent years.[1] Many natural products containing such skeletons have been prepared, and caged or roofed polycyclic compounds have been attractive goals for synthesis.[2-4] More recently, a linear array of cyclopentane rings with a well-defined stereochemistry has been suggested as potential steroid analogues.[5] On the basis of molecular modeling results the linear polyquinane **1** was envisaged as a structural analogue of estrone (**2**). The rather flat backbone of **1** is given by the cis-transoid-cis fusion of the three central cyclopentane rings. The skeleton provides a distance of 9.71 Å between the two oxygen functionalities, which is comparable to that found in estrone (10.74 Å).[6] Superposition of the two skeletons revealed that the rings C and D of **1** require space outside the rings B–C–D of **2** and fill the space of the rings B and C only incompletely.Our primary objective was, therefore, the design of a short and effective synthetic route to **1**. On the basis of retrosynthetic considerations and experimental experience which we had obtained during the synthesis of related structures,[7] we envisaged 6-methoxyindene as a readily accessible starting material for further cyclopentannulations.[8] Addition of one cyclopentene ring would give a benzannulated bicyclo[3.3.0]octene, which could be transformed into the target molecule according to the procedure developed by Oda.[9,10] [2 + 2] photocycloaddition of cyclohex-2-ene-1,4-dione at the exo-side would give an intermediate, which upon treatment with trimethylsilyl iodide would rearrange to the desired compound (Scheme 1). Here we report the synthetic results, which gave **16** as the major and **1** as the minor compound. Comparison of the X-ray structure of **16** with solution data revealed that this compound prefers different conformations in the solid state and in solution.

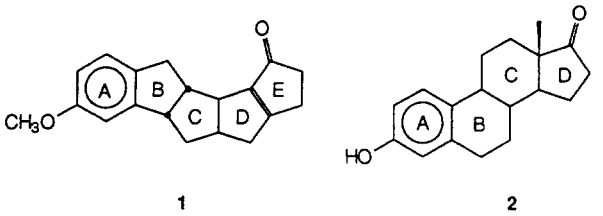

Figure 1.

Results and Discussion

Preparation of the Benzannulated Bicyclo[3.3.0]-octene 9. The route for preparation of the olefin **9**, used as a precursor in the [2 + 2] photocycloaddition, is outlined in Scheme 2. Thus, commercially available 6-methoxyindanone is transformed into the known indene **3**,[11] which underwent a [2 + 2] cycloaddition with in situ generated dichloroketene to give **4**.[12] The regioselective addition is due to the donor properties of the indene being larger in the 2- than in the 1-position. The α,α-dichlorocyclobutanone reacted very rapidly with diazomethane to give in a highly regioselective ring expansion the corresponding α,α-dichlorocyclopentanone **5**, which was dechlorinated with zinc and acetic acid to give **6**[13,14] in high yield.

According to an X-ray structure analysis of **6** the best plane of the indan subunit forms an angle of 67.7° with the best plane of the annulated cyclopentanone ring, which adopts a twist envelope (half-chair) conformation.[15] As expected for this rooflike structure, reduction of the

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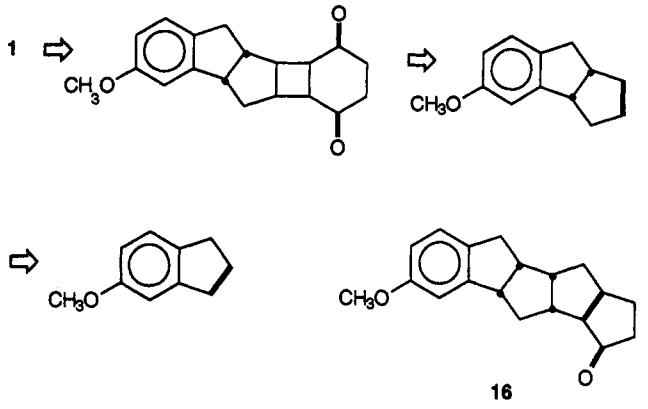
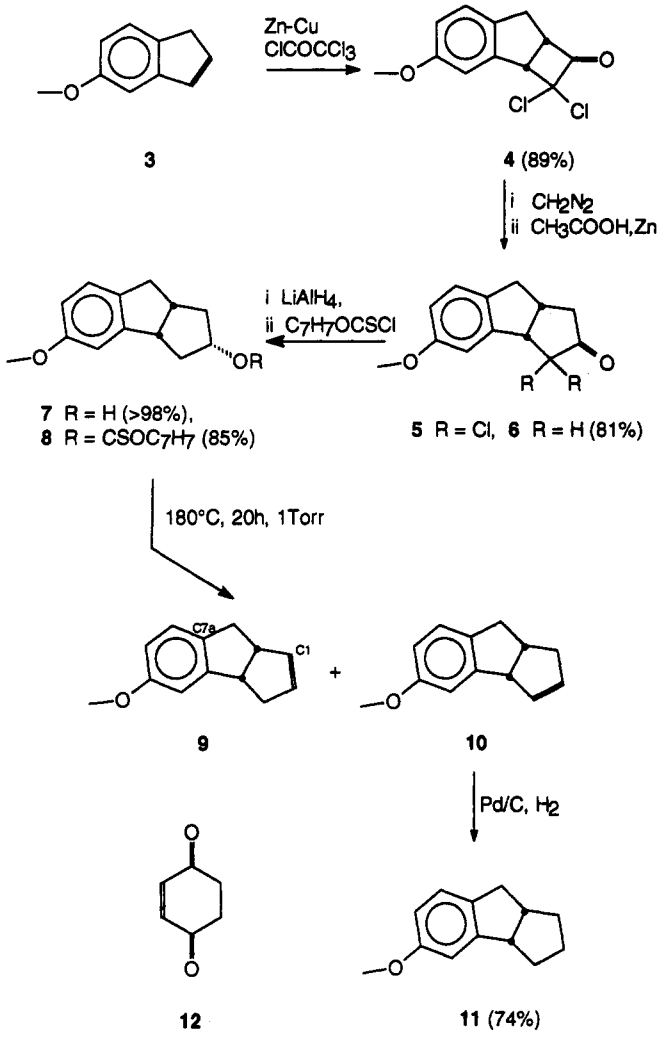
Scheme 1

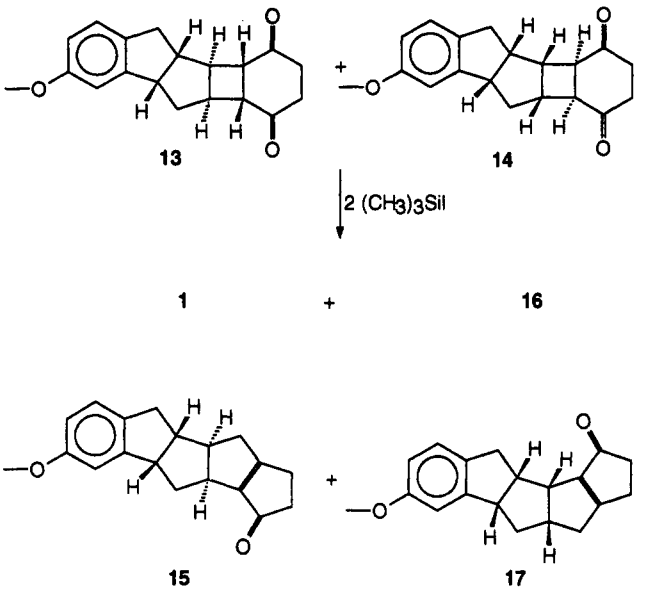


Scheme 2



carbonyl group in **6** by $LiAlH_4$ occurred from the exo-side to give exclusively **7** with an endo hydroxy group. Since dehydration with *p*-toluenesulfonic acid as catalyst was unsuccessful, the carbinol **7** was transformed to the thiono carbonate **8**[16] and thermolyzed to give a mixture of **9** and **10** in a ratio of 1.5:1. Separation of these two isomeric olefins was only successful by chromatography on a silica gel column impregnated with 10% silver nitrate to give **9** in a overall yield (**3** → **9**) of 24%.

Scheme 3



Photocycloaddition of 9. For annulation of **9** by a bicyclo[3.3.0]oct-1(5)-en-2-one moiety the method of Oda[9] was pursued. Contrary to our expectations, irradiation of **9** with cyclohex-2-ene-1,4-dione[17] (**12**) with a high-pressure Hg lamp in dichloromethane and Pyrex glass afforded **13** only as the minor photoproduct (Scheme 3). The major photoproduct was **14** which, purified by chromatography and recrystallization, gave a sample sufficiently pure for structure determination. ^{1}H-NOE experiments revealed a cis-cisoid-cis-transoid-cis structure for **14**.

Final proof for a cis-cisoid-cis structure in **14** was provided by X-ray structure analysis of **16**, obtained from **14** by treatment with trimethylsilyl iodide (see below). The formation of **14** is surprising as it requires the [2 + 2] photocycloaddition between **9** and **12** to occur on the endo-side rather than the exo-side of the bicyclo[3.3.0]-octene ring system. For formulation of a possible mechanism of this unusual intermolecular [2 + 2] photocycloaddition it is relevant that **9** shows a long-wavelength UV absorption at λ_{max} = 369 nm (ϵ = 10.5), which is not present in 5-methoxycyclopenta[*a*]indan (**11**), obtained by hydrogenation of **10** (Scheme 2). Also, the UV spectra of an equimolar mixture of **9** and **12** are to be interpreted in terms of the superposition of the spectra of the individual compounds. This suggests that **9** is photoexcited to give a state where the arene and the double bond interact at the centers C1 and C7a. This intermediate might then react with the π-acceptor molecule **12** in a way that involves the arene-π-system *and* the "free" center of the double bond. The [2 + 2] cycloaddition is eventually achieved by rotation of the complexed **12**.[18]

The crude photoproducts **13** and **14** reacted with two TMSI to give a mixture of the three enones **1**, **15**, and **16** in a ratio of about 1:1:3, which could be separated by HPLC. While **1** and **15** can only be formed from the exo-photoproduct **13**, **16** must arise exclusively from **14**. Since the other isomer **17** to be expected from **14** has not been detected, **14** is transformed into **16** in a highly regioselective process. Due to steric hindrance, attack of TMSI occurs

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(18) Formation of a 1:1 adduct from **9** and maleic anhydride upon irradiation through Pyrex is evidence for the exitation of the bichromophore in **9**.

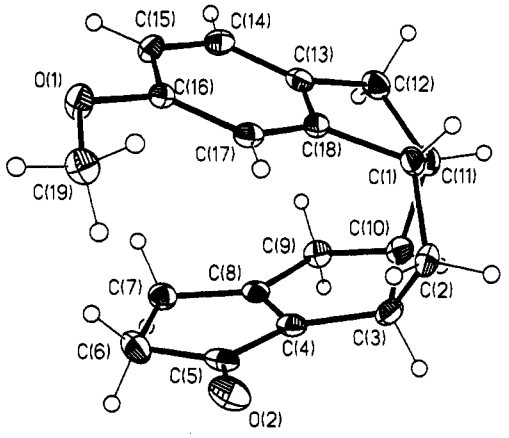


Figure 2. Ortep plot of molecule **16** with atom numbering.

in the case of **14** exclusively at the carbonyl group "anti" to the methoxy substituent, whereas in **13** both carbonyl groups are accessible.[10]

Structures Analysis. NMR results suggested that the major compound isolated from the photocycloaddition and subsequent rearrangement had a structure different from that expected from a [2 + 2] photoaddition on the exo-side. Conclusive evidence was provided by an X-ray structure analysis, which showed that **16** had a U-shaped structure formed by an endo-addition of **12** to **9** during photoreaction.

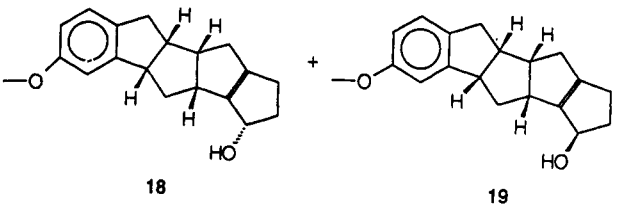
It is evident that the connectivity of the rings B–C–D is cis-cisoid-cis with ring C adopting a C(2) envelope (Figure 2). The torsional angle τ_1 C(9)–C(10)–C(11)–C(12) is only 9.8°, compatible with a long C(10)–C(11) bond of 1.579(4) Å. The U-shaped structure of the molecule is apparent from the short distances of C(5)–C(17) (3.38 Å), C(4)–C(18) (3.13 Å), and C(8)–C(13) (3.45 Å), all values being smaller than those found between the layers in graphite (3.40 Å).[19] The short distances between C(8) and C(13) as well as C(5) and C(17) suggest a π-donor–acceptor interaction between the aromatic ring and the enone-π-system, which might be counterbalanced by the torsional strain associated with ring C (see below).

^{1}H-NOE experiments of **16** in solution do not confirm the U-shaped structure found in the solid state. For an U-shaped conformation significant ^{1}H-NOE effects had to be expected for C(15)–H and C(6)–H_{endo}. In view of the absence of these interactions and the observation of ^{1}H-NOE effects from one of the C(2)-H's to C(17)-H and from C(1)-H to C(3)-H and C(10)-H an opened-out rather than a U-shaped structure for **16** must be prevalent in solution. Model studies suggest that the conformation of ring C changes readily from an "exo"-C(2)-envelope to an "endo"-C(2)-twist envelope.

This hypothesis is supported by the observation that reduction of **16** with $LiAlH_4$ in ether gives a 1:1 mixture of the two diastereomeric carbinols **18** and **19** (GC–MS). If the solid state conformation of **15** would have been preserved in solution, only the endo-alcohol **18** should have been formed (Scheme 4).

Computational Results. In order to gain a coherent perspective for the unique structural and chemical behavior of **16**, force field calculations using Allinger's MM2 program[20] were performed. The torsional energy surface

Scheme 4



of molecule **16** (Figure 3) was obtained by changing the two dihedral angles τ_2 C(9)–C(10)–C(3)–C(2) and τ_3 C(12)–C(11)–C(1)–C(2) by increments of 5°. The resulting 17 × 19 values, containing three local minima, were splined to a 81 × 91 grid using the PC-software package SURFER.[21]

One of the three local minima (LM1), which were fully optimized, is structurally very close to the X-ray structure (see Figure 4 and Table 1). The remaining two structures LM2 and LM3 are best described by open conformations. Opening of the torsional angle τ_1 C(9)–C(10)–C(11)–C(12) maintaining ring C in an "exo"-C(2)-twist envelope conformation leads to the local minimum LM2, whereas LM3 is formed from LM2 by a conformational change in ring C leading to an "endo"-C(2)-envelope. The HOF's and the strain energies of these three conformers differ by less than 3.1 kJ/mol from LM1 and from LM3 by only 1.84 kJ/mol. Furthermore, our MM2 results suggest that the conformational change LM1 → LM2 → LM3 follows very closely the pseudorotation of a cyclopentane, with rotational barriers in the range of about 10–12 kJ/mol.[22]

Conclusion

In the course of the synthesis of a cyclopentanoid steroid analogue a novel photoinduced [2 + 2] cycloaddition at the endo-side of a benzannulated bicyclo[3.3.0]oct-2-ene was observed. Thus, an efficient preparative route to tricyclic compounds with a cis-cisoid-cis skeleton has been established. The benzannulated tetraquinane with a central cis-cisoid-cis triquinane, prepared by ring rearrangement, shows different structures in the solid state and in solution. According to MM2 results, the conformational space of the central cis-cis-cis tetrasubstituted cyclopentane is best described by a partial, low-energy pseudorotation.

Experimental Section

General Procedures. Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. IR and NMR spectra were measured in $CHCl_3$ and $CDCl_3$. Infrared spectra were recorded on a Perkin-Elmer 782 infrared spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) spectrometer. ^{1}H NOE spectra were recorded on a Bruker AM400 spectrometer. Chemical shifts are given in ppm relative to internal TMS δ (0.00); J's are given in Hz. Mass spectra (MS) were determined on a Varian MAT CH7A spectrometer and are reported in units of

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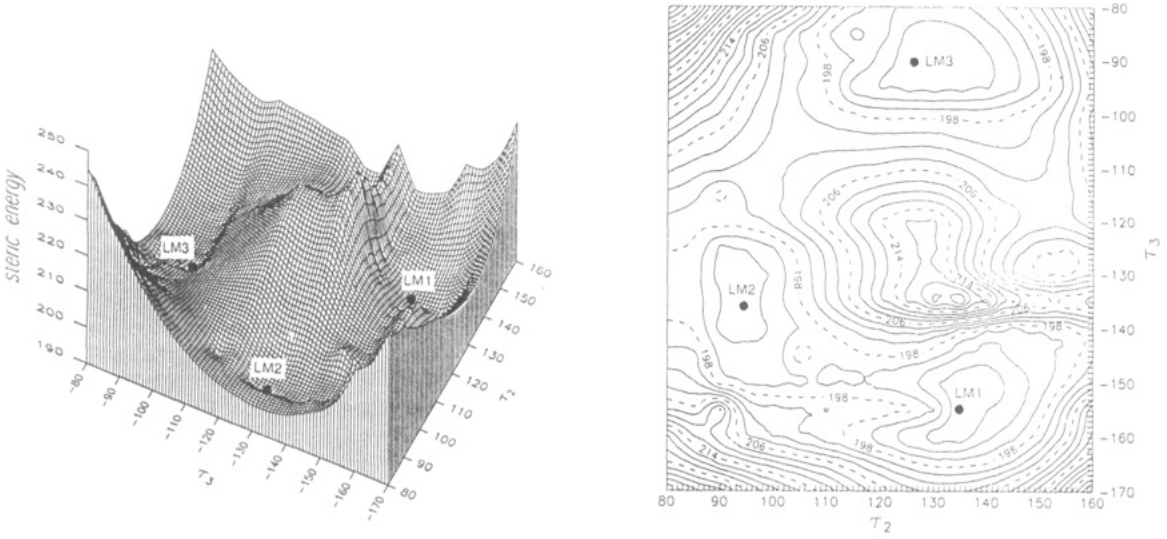

Figure 3. MM2-generated energy surface in relationship to the torsional angles τ_2 C(9)–C(10)–C(3)–C(2) and τ_3 C(12)–C(11)–C(1)–C(2) in steps of 5° for the range +80° to +160° and −80° to −170° respectively. Isoenergetic lines are separated by 2 kJ/mol intervals. (Left) perspective view. (Right) contour map.

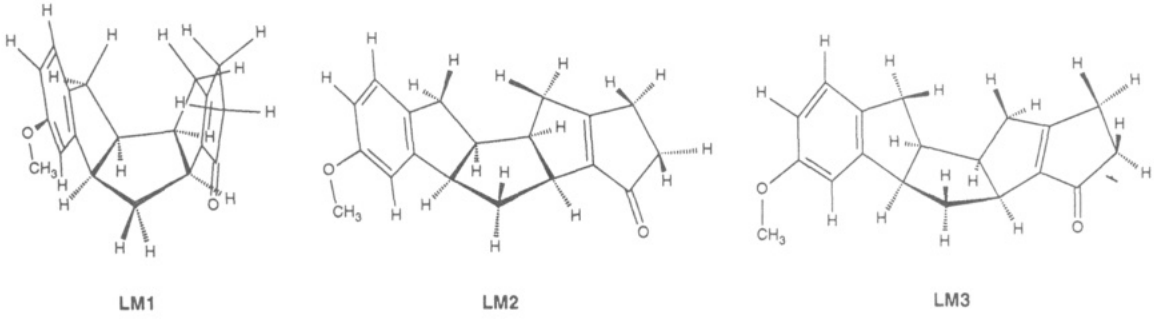

Figure 4. MM2 structures of open (LM2 and LM3) and U-shaped (LM1) conformations of **16**.

Table 1. Selected X-ray Structural Data for 16 and MM2 Results for the Three Local Minima LM1, LM2, and LM3[a]

	conform. of ring C[b]	dihedral angles τ_1	τ_2	τ_3	HOF	steric energy	strain energy
X-ray **16**	e	9.8	134.0	−154.1			
LM1	e	9.5	135.1	−155.4	−7.07	190.8	157.7
LM2	tw e	28.5	94.9	−135.9	−5.23	192.5	159.4
LM3	e	−27.5	126.5	−89.8	−8.28	189.5	156.5

[a] Local conformation, dihedral angles (deg) τ_1 C(9)–C(10)–C(11)–C(12); τ_2 C(9)–C(10)–C(3)–C(2); τ_3 C(12)–C(11)–C(1)–C(2); HOF, steric and strain energies in kJ/mol. [b] e = envelope; tw e = twist envelope.

m/z and in relative intensities to the base peak. HRMS and GC–MS were performed on a VG Autospec spectrometer. Elemental analyses were performed by Labo Chimie pharmaceutique, Université de Genève. Reactions were normally performed under an N_2 atmosphere. The solutions were dried over $MgSO_4$. HPLC was conducted by using a 7-μm silica gel column (250 × 23mm) with a Uvikon 720 LC as detector and hexane/2-propanol (azeotrope) as mobile phase, flow rate 1.4 mL/min. Zn–Cu complex,[12] 0.2 M diazomethane solution in ether,[14] and cyclohex-2-ene-1,4-dione[16] were prepared according to literature procedures. Other chemicals were purchased from commercial suppliers and used without further purification.

Crystal Structure Determination of Compound 16. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer at 110 K. $C_{19}H_{21}O_4$, M_w = 280.366, $P2_1/c$, a = 7.804(5) Å, b = 25.341(7) Å, c = 7.577(3) Å, β = 111.06°(3), Z = 4, d_x = 1.332 g/cm^3, V = 1398.4(11) Å^3. A total of 2715 reflections were scanned and reduced in a unique set of 1773 reflections with $I > 3.0(I)$. The structure was solved by using direct method with SHELXS-86[23] and refined with SHELX76.[23] Convergence was reached at R = 0.055. Hydrogen atoms were introduced at calculated positions.[24]

***cis*-2,2-Dichloro-4-methoxy-2,2a,7,7a-tetrahydrocyclobuta[*a*]inden-1-one (4).** To a solution of 6-methoxyindene (8 g, 54.9 mmol) in 80-mL of anhydrous ether was added freshly prepared Zn–Cu complex (4.13 g, 62.8 mmol). After dropwise addition of trichloroacetyl chloride (11.36 g, 62.4 mmol) and phosphorus oxychloride (9.57 g, 62.4 mmol) in 100 mL of anhydrous ether, the mixture was heated to 80 °C for 3 h. Filtration through Celite and concentration in vacuo gave a solution (50 mL) which was treated twice with pentane and decanted. The precipitate was treated with hot ether and pentane. The combined extracts were washed with water, saturated $NaHCO_3$, and brine, dried, and concentrated to give 13.61 g (89%) of **4** as white crystals: mp 70-71 °C (ether); ^{1}H NMR 3.11 (dd, J = 16.5, 7.5, 1H), 3.32 (d, J = 16.5, 1H), 3.82 (s, 3H), 4.48 (m, 2H), 6.88 (dd, J = 9.0, 1.8 , 1H), 6.94 (d, J = 1.8, 1H), 7.14 (d, J = 9.0, 1H); ^{13}C NMR 33.5, 55.5, 58.9, 59.9, 88.1, 112.8, 116.1, 125.9, 135.3, 138.8, 159.4, 197.5; IR 1810 (s), 1625 (m), 1615 (m), 1495 (s), 1240 (s); MS 258 (M + 2, 31), 256 (M$^+$, 31), 193 (96), 158 (74), 146 (100), 131 (30), 115 (36); HRMS m/z calcd for $C_{12}H_{10}O_2Cl_2$ 256.005 785, found 256.005 43. Anal. Calcd for $C_{12}H_{10}O_2Cl_2$: C, 56.05; H, 3.92; Cl, 27.57. Found: C, 56.14; H, 3.96; Cl, 27.80.

***cis*-3,3-Dichloro-–5-methoxy-3,3a,8,8a-tetrahydro-1*H*-cyclopenta[*a*]inden-2-one (5).** To a solution of **4** (8 g, 31.2 mmol) in 50 mL of ether was added dropwise diazomethane (311 mL of

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(24) The author has deposited atomic coordinates for **16** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

0.2 M in ether, 62.2 mmol) and methanol (1 mL). After 30 min the reaction was quenched with acetic acid and the solvent evaporated. Flash chromatography with ethyl acetate/hexane (1:10) gave white crystals of **5** (7.7 g, 92%): mp 83 °C (ether); R_f = 0.27; ^{1}H NMR 2.46 (dd, J = 20, 5, 1H), 2.79 (dd, J = 15, 5, 1H), 2.95 (dd, J = 20, 10, 1H), 3.25 (m, 2H), 3.80 (s, 3H), 4.20 (d, J = 8.4, 1H), 6.85 (dd, J = 8.4, 2.4, 1H), 7.15 (m, 2H); ^{13}C NMR 36.0, 37.8, 38.5, 55.5, 61.6, 87.8, 112.1, 115.1, 125.7, 136.1, 139.3, 159.1, 201.3; IR 1770 (s), 1610 (s), 1585 (m), 1490 (s), 1465 (s), 1445 (s), 1430 (m), 1295 (s), 1240 (s); MS 272 (M + 2, 29), 270 (M^+, 44), 235 (32), 219 (55), 194 (90), 159 (61), 145 (46), 134 (62), 121 (100), 91 (38); HRMS m/z calcd for $C_{13}H_{12}O_2Cl_2$ 270.021 435, found 270.021 67.

***cis*-5-Methoxy-3,3a,8,8a-tetrahydro-1*H*-cyclopenta[*a*]inden-2-one (6).** A mixture of **5** (7.7 g, 28.5 mmol) and zinc powder (12.1 g, 0.185 mmol) in pure acetic acid (104 mL, 1.73 mmol) was kept at 70 °C for 2 h. After filtration through Celite, the solution was added to water and extracted with ether. The ether extracts were washed with saturated $NaHCO_3$ and brine, dried, and evaporated to give **6** (5.1 g, 89%) as a white solid: mp 96 °C (ether); ^{1}H NMR 1.97 (dd, J = 19.2, 7.5, 1H), 2.53 (m, 2H), 2.63–2.79 (m, 2H), 3.17 (m, 2H), 3.78 (s, 3H), 3.84 (m, 1H), 6.72 (m, 1H), 6.74 (dd, J = 8.1, 0.75, 1H), 7.14 (d, J = 8.1, 1H); ^{13}C NMR 37.6, 40.0, 43.4, 43.9, 46.2, 55.4, 110.1, 113.2, 125.9, 134.1, 146.5, 159.3, 219.1; IR 1735 (s), 1610 (m), 1585 (m), 1490 (s), 1465 (w); MS 202 (M^+, 78), 186 (16), 159 (100), 145 (64), 128 (26), 115 (38), 91 (12); HRMS m/z calcd for $C_{13}H_{14}O_2$ 202.099 380, found 202.098 88;

***cis*-5-Methoxy-1,2,3,3a,8,8a-hexahydrocyclopenta[*a*]inden-2-ol (7).** Reduction of **6** (3.5 g, 17.3 mmol) in 100 mL of absolute ether with lithium aluminium hydride (1.32 g, 34.6 mmol) at −20 °C gave after workup pure **7** (3.47 g, >98%) as a colorless oil: ^{1}H NMR 1.43 (m, 2H), 1.75 (ddd, J = 13.0, 5.0 5.0, 1H), 2.2 (dddd, J = 16, 9, 5, 1.5, 1H), 2.36 (dddd, J = 16, 9, 5, 1.5, 1H), 2.76 (dd, J = 15, 3, 1H), 2.88 (m, 1H), 3.16 (dd, J = 15, 8, 1H), 3.55 (m, 1H), 3.75 (s, 3H), 4.25 (m, 1H), 6.70 (m, 2H), 7.10 (d, J = 7.5, 1H); ^{13}C NMR 38.6, 40.5, 42.1, 43.2, 48.6, 55.4, 75.0, 109.6, 112.9, 125.5, 134.2, 149.4, 159.1; IR 3620 (m), 3580 (w), 1615 (m), 1500 (s), 1475 (m), 1450 (w), 1440 (w), 1290 (m); MS 204 (M^+, 40), 186 (58), 171 (14), 158 (20), 145 (100), 115 (20), 102 (10), 84 (24), HRMS m/z calcd for $C_{13}H_{16}O_2$ 204.115 030, found 204.115 11.

***O*-(5-Methoxy-1,2,3,3a,8,8a-hexahydrocyclopenta[*a*]inden-2-yl) *O*-*p*-Tolyl Thionocarbonate (8).** Esterification of alcohol **7** (3.47 g, 17 mmol) with *O*-4-methylphenyl chlorothioformate (6.03 g, 32.3 mmol) in 40 mL of dry pyridine gave after workup and MPLC with ethyl acetate/petrol ether (1:10) **10** (5.1 g, 85%) as yellowish crystals: mp 84–85 °C (ether/hexane); R_f = 0.65; ^{1}H NMR 1.76 (m, 1H), 2.14 (ddd, J = 13.8, 5.2, 5.2, 1H), 2.35 (s, 3H), 2.45 (m, 1H), 2.66 (ddd, J = 13.8, 8.7, 6.6, 1H), 2.77 (dd, J = 15.5, 2.3, 1H), 2.97 (m, 1H), 3.18 (dd, J = 15.5, 5.2, 1H) 3.67 (m, 1H), 3.80 (s, 3H), 5.56 (m, 1H), 6.73 (d, J = 8, 2H), 6.85 (d, J = 8, 2H), 7.07 (d, J = 9, 1H), 7.16 (d, J = 9, 2H); ^{13}C NMR 20.9, 37.9, 38.1, 38.6, 40.5, 48.0, 55.4, 86.7, 109.6, 112.8, 121.5, 125.4, 129.9, 134.0, 136.1, 148.6, 151.2, 159.1, 194.8; IR 1615 (m), 1590 (w), 1510 (m), 1500 (s), 1290 (s), 1200 (s), 910 (s); MS 354 (M^+, 46), 310 (13), 247(19), 242 (20), 230 (22), 186 (100), 159 (43), 145 (52), 121 (30), 108 (31), 91 (40); HRMS m/z calcd for $C_{21}H_{22}O_3S$ 354.128 967, found 354.129 460.

***cis*-5-Methoxy-3,3a,8,8a-tetrahydrocyclopenta[*a*]indene (9).** Solid **8** (5.1 g, 14.4 mmol) was pyrolyzed at 180 °C under reduced pressure (ca. 20 Torr). The crude product was dissolved in ether, washed with 2 N NaOH and brine, and dried. Flash chromatography with ether/hexane (1:5) through a short column afforded a yellow oil, which was further purified by MPLC with the same eluant over silica gel coated with 10% silver nitrate to yield **9** (1.2g, 44.5%) and **10** (0.6g, 22.3%) as oils. **9**: bp 120 °C/0.1 Torr; R_f = 0.13; ^{1}H NMR 2.51 (m, 1H), 2.78 (d, J = 14.8, 1H), 2.86 (m, 1H), 3.13 (dd, J = 14.8, 8.8, 1H), 3.57 (m, 1H), 3.77 (s, 3H), 3.79 (m, 1H), 5.62 (m, 2H), 6.72, (ddd, J = 9.1, 1.8, 1.0, 1H), 6.76 (d, J = 1.8, 1H), 7.06 (d, J = 9.1, 1H); ^{13}C NMR 36.7, 39.9, 47.6, 49.6, 55.4, 109.7, 112.9, 125.3, 129.1, 134.1, 134.6, 149.2, 158.9; IR 1610 (m), 1590 (w), 1495 (s), 1470 (m), 1445 (m); MS 186 (M^+, 100), 171 (30), 158 (30), 155 (20), 145 (92), 128 (32), 115 (40); HRMS m/z calcd for $C_{13}H_{14}O$ 186.104 465, found 186.104 25.

***cis*-5-Methoxy-1,3,8,8a-tetrahydrocyclopenta[*a*]indene (10):** bp 95–100 °C/0.1 Torr; R_f = 0.43; ^{1}H NMR 2.14–2.26 (m, 1H), 2.56–2.78 (m, 2H), 3.20 (m, 2H), 3.78 (s, 3H), 4.20 (m, 1H), 5.68 (m, 1H), 5.79 (m, 1H), 6.70 (dd, J = 10, 3.8, 1H) 6.76 (d, J = 3.8, 1H), 7.05 (d, J = 10, 1H); ^{13}C NMR 39.5, 40.4, 41.0, 55.4, 58.0, 109.4, 112.5, 125.2, 130.1, 132.0, 134.9, 146.4, 158.9; IR 1605 (m), 1585 (m), 1490 (s), 1460 (m), 1445 (m); MS 186 (M^+, 100), 171 (25), 158 (44), 145 (58), 128 (26), 121 (62), 115 (32), 108 (38); HRMS m/z calcd for $C_{13}H_{14}O$ 186.104 465, found 186.104 68.

***cis*-5-Methoxy-1,2,3,3a,8,8a-hexahydrocyclopenta[*a*]indene (11).** To a solution of **10** (150 mg, 0.8 mmol) in 10 mL of absolute methanol was added 10% Pd/C (10 mg), and a stream of hydrogen was passed through the solution for 3 h. Filtration through Celite and MPLC chromatography with ether/hexane (1:5) gave **11** (112 mg, 74%) as an oil: R_f = 0.57; ^{1}H NMR 1.27–1.62 (m, 3H), 1.72 (m, 1H), 1.85 (m, 1H), 2.00 (m, 1H), 2.59 (dd, J = 15, 3, 1H), 2.88 (m, 1H), 3.13 (dd, J = 15, 9, 1H), 3.58 (m, 1H), 3.80 (s, 3H), 6.69 (m, 2H), 7.03 (d, J = 9, 1H); ^{13}C NMR 26.1, 34.0, 34.9, 38.7, 42.7, 50.5, 55.4, 109.6, 112.4, 124.8, 135.5, 149.6, 159.0; IR 1615 (m), 1595 (w), 1500 (s), 1470 (m), 1455 (m); MS 188 (M^+, 100), 173 (17), 159 (96), 146 (30), 128 (84), 114 (72), 101 (40).

Photoreaction of 9. A mixture of **9** (625 mg, 3.3 mmol) and cyclohex-2-ene-1,4-dione (**12**) (740 mg, 6.7 mmol) in 18 mL of dry dichloromethane was irradiated for 2.5 h with a Heraeus TQ150 high-pressure Hg lamp. Evaporation of the solvent and flash chromatograpy with ethyl acetate/hexane (1:2) gave a mixture of crude **13** and **14** (1.0 g, 100%), which is used directly for ring rearrangement. Pure **13** could be isolated by MPLC performed with the same eluant and crystallization from ether/hexane to give slightly brown crystals of ***cis-cisoid-cis-transoid-cis*-14-Methoxypentacyclo[9.7.0.0^{2,9}.0^{3,8}.0^{12,17}]octadeca-12,14,16-triene-4,7-dione (14):** mp 93 °C (ether/hexane); R_f = 0.2; ^{1}H NMR 2.28 (m, 2H), 2.39 (dd, J = 9,3.8, 1H), 2.55–2.85 (m, 5H), 2.89 (d, J = 16.3, 1H), 2.96–3.09 (m, 3H), 3.15 (dd, J = 16.3, 6.8, 1H), 3.81 (s, 3H), 3.85 (m, 1H), 6.74 (dd, J = 8.3, 2.8, 1H), 6.82 (d, J = 8.3, 1H), 7.10 (d, J = 8.3, 1H); ^{13}C NMR 33.5, 36.6, 37.5, 37.8, 43.9, 44.1, 46.1, 47.6, 49.5, 53.2, 55.4, 109.2, 113.2, 124.9, 135.3, 147.9, 159.2, 209.8, 210.5; IR 1710 (s), 1610 (m), 1490 (m), 1330 (w), 1295 (w), 1265 (m); MS 296 (M^+, 6), 261 (44), 199 (6), 141 (13), 110 (100), 81 (34), 55 (16); HRMS m/z calcd for $C_{19}H_{20}O_3$ 296.141 245, found 296.141 17.

Ring Rearrangement of 13 and 14. To a solution of **13** and **14** (1.0 g, 3.3 mmol) in 40 mL of dry dichloromethane was added quickly TMSI (1.5 g, 7.5 mmol) under N_2. After the mixture was stirred for 6 h, 100 mL of dichloromethane was added, and the solution was extracted with 2 N K_2CO_3. Workup and MPLC chromatography with ethyl acetate/hexane (1:1) gave a mixture of **1**, **15**, and **16** (410 mg, 44%, R_f = 0.5) as a colorless viscous oil. HPLC chromatography of this oil afforded ***cis-transoid-cis*-14-Methoxypentacyclo[9.7.0.0^{2,9}.0^{3,7}.0^{12,18}]octadeca-3,12,14,16-tetraen-4-one (1)** (73 mg, 8%): mp 114 °C (ether); ^{1}H NMR 1.7 (m, 1H), 2.25 (d, J = 19, 1H), 2.35 (m, 1 H), 2.48 (broad s, 2H), 2.62 (dd, J = 19, 7.3, 1H), 2.69–2.76 (m, 2H), 2.76–2.90 (m, 3H), 2.90 (d, J =15.6, 1H), 3.18 (dd, J = 15.6, 7.3, 1H), 3.56 (m, 1H), 3.78 (s, 3H), 6.70 (m, 2H), 7.10 (d, J = 9.1, 1H); ^{13}C NMR 25.7, 38.0, 38.9, 39.6, 41.2, 47.2, 48.1, 52.0, 52.2, 55.4, 109.2, 112.2, 125.3, 135.5, 147.5, 150.8, 158.9, 184.5, 204.2; IR 1690 (s), 1640 (m), 1615 (w), 1495 (m), 1390 (w), 1225 (s); MS 280 (M^+, 100), 265 (6), 251 (5), 237 (4), 223 (8), 209 (5), 185 (48), 172 (15), 160 (22), 146 (10), 133 (17), 121 (15), 115 (17); HRMS m/z calcd for $C_{19}H_{20}O_2$ 280.146 330, found 280.146 39.

***cis-transoid-cis*-16-Methoxypentacyclo[9.7.0.0^{3,10}.0^{4,8}.0^{12,18}]-octadeca-4,13,15,17-tetraen-5-one (15)** (75 mg, 8%): mp 153 °C (ether); ^{1}H NMR 2.12 (ddd, J = 13.3, 8.4, 4.8, 1H), 2.25 (ddd, J = 13.3, 8.4, 4.8, 1H), 2.40 (d, J = 17, 1H), 2.50 (m, 2H), 2.58 (m, 1H), 2.67–2.90 (m, 5H), 3.07 (dd, J = 17, 8, 1H), 3.18 (broad s, 1H), 3.51 (m, 1H), 3.77 (s, 3H), 6.71 (m, 2H), 7.07 (d, J = 9, 1H); ^{13}C NMR 25.7, 35.3, 37.5, 39.0, 41.2, 45.1, 51.9, 53.8, 55.1, 55.4, 109.5, 112.5, 125.3, 134.3, 148.3, 150.9, 159.0, 185.1, 204.0; IR 1685 (s), 1635 (m), 1625 (m), 1490 (m), 1390 (m); MS 280 (M^+, 100), 265 (6), 251 (4), 237 (4), 223 (9), 209 (4), 185 (38), 172 (16), 160 (24), 146 (16), 133 (13), 121 (20); HRMS m/z calcd for $C_{19}H_{20}O_2$ 280.146 330, found 280.146 18.

***cis-cisoid-cis*-16-Methoxypentacyclo[9.7.0.0^{3,10}.0^{4,8}.0^{12,18}]-octadeca-4,13,15,17-tetraen-5-one (16)** (223 mg, 24%): mp 96 °C (ether/dichloromethane (10:1)) ^{1}H NMR 1.88 (m, 1H), 2.10–2.36 (m, 5H), 2.41–2,54 (m, 2H), 2.74 (d, J = 12.4, 1H), 2.9–3.05

(m, 2H), 3.36 (m, 2H), 3.60 (m, 1H), 3.78 (s, 3H), 6.59 (ddd, J = 9.3, 2.8, 1.0, 1H), 6.63 (d, J = 2.8, 1H), 7.02 (d, J = 9.3, 1H); ^{13}C NMR 25.2, 33.3, 33.5, 34.1, 41.0, 45.6, 48.2, 50.6, 52.9, 55.4, 108.3, 112.9, 124.5, 134.9, 148.9, 150.6, 158.7, 186.7, 203.8; IR 1685 (s), 1635 (m), 1610 (w), 1490 (m); MS 280 (M^+, 100), 265 (5), 252 (7), 237 (5), 223 (7), 209 (5), 197 (6), 159 (35), 146 (30), 133(25), 120 (18); HRMS m/z calcd for $C_{19}H_{20}O_2$ 280.146 330, found 280.146 580. Anal. Calcd for $C_{19}H_{20}O_2$: C, 80.30; H, 7.19. Found: C, 80.26; H, 7.18.

Reduction of 16. Reaction of **16** (20 mg, 0.07 mmol) with $LiAlH_4$ (5.4 mg, 0.14 mmol) in 5 mL of anhydrous ether at −20 °C for 30 min gave after workup a mixture of alcohols **18** and **19** (20 mg) as a viscouse oil: GC–MS 264 ($M^+ - 18, - H_2O$, 100), 249 (6), 236 (7), 223 (13), 210 (7), 198 (11), 159 (43), 146 (45), 128 (17), 117 (45), 115 (43), 104 (31), 91 (29), 77 (22); and 264 ($M^+ - 18, - H_2O$, 100), 249 (6), 236 (7), 172 (13), 159 (50), 146 (46), 131 (14), 128 (14), 117 (72), 115 (43), 104 (28), 91 (33), 77 (20).

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Supplementary Material Available: ^1H and ^{13}C NMR of compounds **1**, **4–11**, and **14–16** (24 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.