# 135. Setting the Bridgehead Oxidation Level in *trans*-Tricyclo[9.3.1.$0^{3,8}$]pentadecanes as a Prelude to the Dual Synthesis of Taxol and Taxusin[1])

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The key elements associated with the synthetic elaboration of functionalized *trans*-tricyclo-[9.3.1.$0^{3,8}$]pentadecanes carrying either a bridgehead H or OH substituent are detailed. Starting with **12**, a ketone available in two steps from (*R*)-2-oxo-7,7-dimethyl-1-vinylbicyclo[2.2.1]heptane, it proved possible to introduce *trans*-B/C ring juncture configuration as in **16** in five steps. This advanced intermediate constitutes the point of bifurcation. The pathway to taxusin precursor **23** was attained by stereospecific osmylation, reduction, and pinacol-like 1,2-*Wagner-Meerwein* rearrangement within acetoxy mesylate **22c**. Still more abbreviated is the route to **32**, which again takes advantage of the osmylation step but proceeds forward without reduction of the rear carbonyl group. Once hydroxy diketone **31** is produced, equilibration in the presence of $(t\text{-BuO})_3Al$ results in complete conversion to **32**. The many stereoselective transformations developed in the course of this study, in combination with the several thermodynamic questions that have been clarified, are expected to be highly serviceable as more advanced thrusts toward taxusin and taxol are mounted.

**Introduction.** – Previous accounts from this laboratory have dealt with the design and development of a convergent strategy for the eventual synthesis of taxane diterpenes [1]. These and more recent studies [2] have established the feasibility of incorporating within a carbinol such as **1** the proper number of oxygenated centers essential to ultimate construction of the target molecules. Since both epimers of **1** undergo anionic oxy-*Cope* rearrangement specifically *via endo*-chair transition states [1e], readily available ketones such as **2** and **2′** serve as convenient precursors to the important *cis*-tricyclo-[9.3.1.$0^{3,8}$]pentadecanes **3** and **4** (*Scheme 1*) [1e]. While the optical purity of these intermediates is very high and their absolute configuration appropriate, several crucial issues remain to be addressed. One of these is the establishment of the *trans*-B/C configuration common to all taxanes (for reviews, see [3]). Since the *trans*-isomers are generally more thermodynamically stable than their *cis*-counterparts (MM2 calculations [4] and experiment [5]), one can consider epimerization following arrival at **2** (**2′**) or only after **3** and **4** have been accessed. The latter tactic must avoid a situation where internal aldolization can operate [1e], since stereochemical crossover is thereby precluded. In this paper, we detail the consequences of setting the requisite *trans*-relationship in **2**/**2′** on the outcome of those 1,2-shifts previously shown to be notably effective at delivering **3** and **4** [1e].

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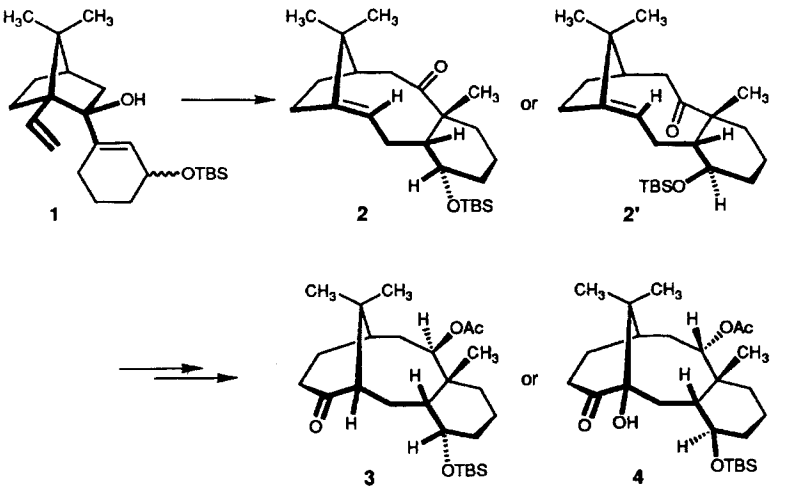
[1]) Originally presented in a lecture at the meeting celebrating the 100th Anniversary of the Geneva Conference: 'Organic Chemistry: Its Language and Its State of the Art', Geneva, April 22–24, 1992.

[2]) Chemistry Department Fellow, 1988–1989; National Needs Fellow, 1991–1992.

*Scheme 1*

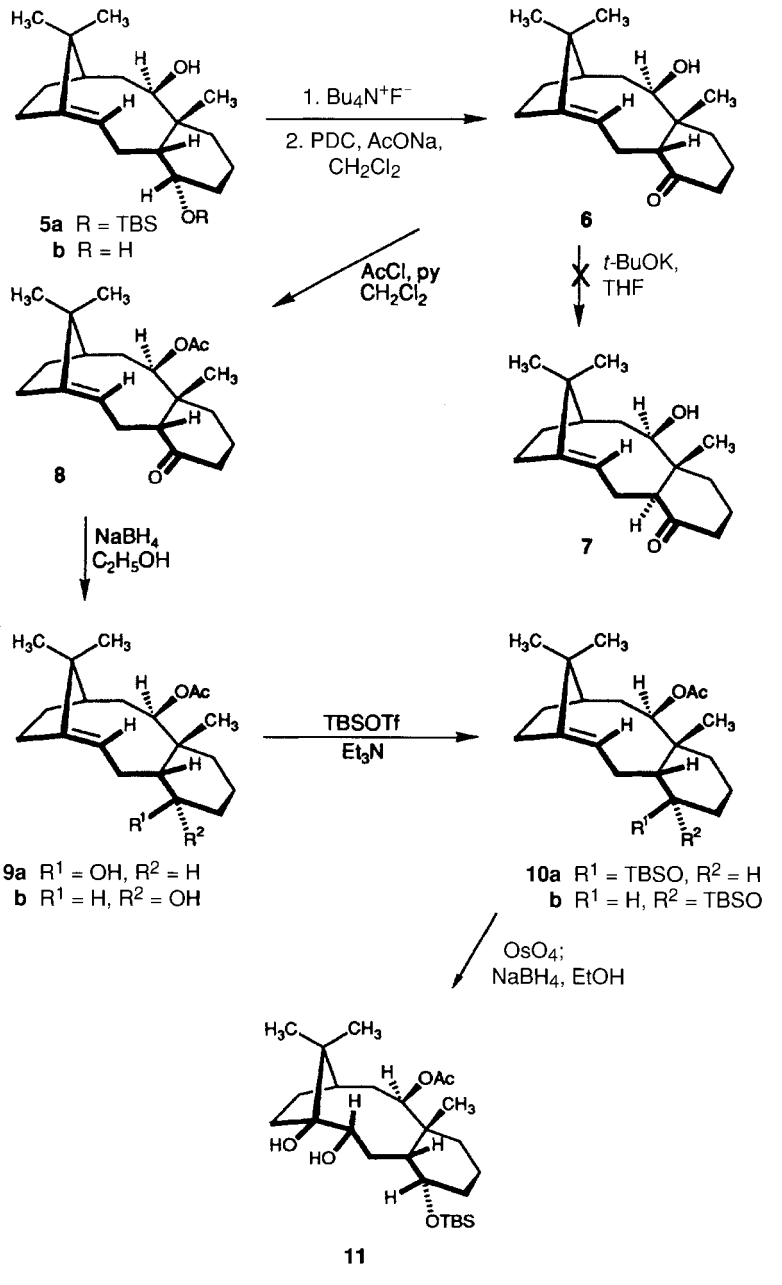



TBS = (*t*-Bu)$Me_2$Si

**Results and Discussion.** – *Epimerization Studies.* With the above goal in mind, optically pure **5a** [1e] was desilylated and treated with pyridinium dichromate (PDC) in the presence of AcONa as buffer. The substantial difference in steric accessibility to the pair of OH groups in **5b** was utilized to advantage in obtaining a single hydroxy ketone in highly regioselective fashion (91%; *Scheme 2*). The high-field $^1$H-NMR spectrum of this product was consistent with its formulation as either **6** or **7**. Its inertness toward strong bases such as *t*-BuOK or MeONa was initially construed to be an indication that the desired epimerization occurred spontaneously during the oxidation procedure [1d]. However, molecular-mechanics calculations [6], involving the global-minimum-energy conformations of this pair of ketones, suggested subsequently that the thermodynamic bias in this instance may well reside in favor of **6** (*Fig. 1, a*; $E_S = 55.9$ kcal/mol, $E_T = 66.8$ kcal/mol) rather than **7** (*Fig. 1, b*; $E_S = 58.7$ kcal/mol, $E_T = 69.6$ kcal/mol) as originally projected.

Convincing proof of B/C ring-juncture configuration was, therefore, required. To this end, the hydroxy ketone was acetylated and reduced with $NaBH_4$ prior to formation of the (*tert*-butyl)dimethylsilyl ethers. The reduction step afforded chromatographically separable $\alpha$- and $\beta$-epimers, and these were independently silylated. The existence of 1,3-diaxial nonbonded interactions involving the proximate angular Me group and incoming borohydride was expected to exceed the energy costs associated with the torsional strains that develop during equatorial attack. That **9a** is indeed the major product (ratio 2.5:1) was deduced initially by analysis of the prevailing spin interactions to the respective carbinol protons. In **9a**, the broadened *singlet* of this signal at 3.88 ppm conforms to its equatorial orientation with resultant low-level coupling to neighboring vicinal protons. In contrast, the two *trans*-diaxial couplings in **9b** are reflected in its appearance as a widely separated triplet of *doublets* ($J = 4.2$, 12.1 Hz) at 3.82 ppm. This conclusion was corroborated by the independent preparation of **10b** by acetylation of **5a**.

*Scheme 2*




**5a** R = TBS
**b** R = H

**6**

**7**

**8**

**9a** $R^1$ = OH, $R^2$ = H
**b** $R^1$ = H, $R^2$ = OH

**10a** $R^1$ = TBSO, $R^2$ = H
**b** $R^1$ = H, $R^2$ = TBSO

**11**

Ultimately, **10b** was subjected to osmylation. The resultant diol necessarily had to be **11**, since it differed intrinsically from the B/C *trans*-isomer that was later prepared by the alternate route to be described below. Accordingly, **6** is clearly recalcitrant to equilibrate with its *trans*-isomer **7**.

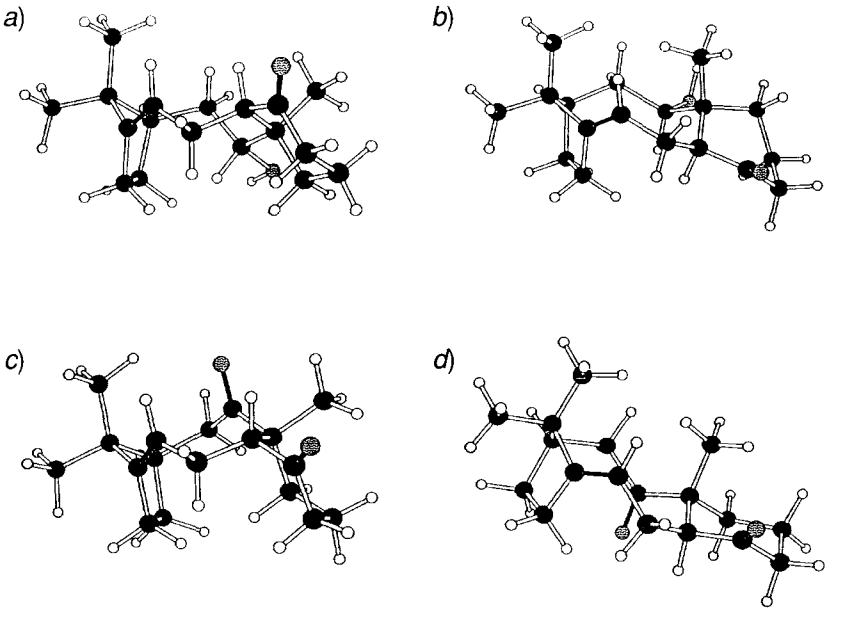



Fig. 1. *Global-minimum-energy conformations of* a) *the hydroxy ketone* **6**; b) *the hydroxy ketone* **7**; c) cis-*diketone* **14**; *and* d) trans-*diketone* **15** (Chem 3-D output). The silyl groups have been omitted to simplify matters.

To the extent that MM2 calculations involving these tricyclic medium-ring compounds can be relied upon to provide guidance regarding relative thermodynamic stabilities, diketones **14** and **15** had necessarily to be viewed with particular interest. For these structures, the data inferred that simple modulation of C(5) from $sp^3$ to $sp^2$ hybridization effectively switches the ordering of both $E_S$ and $E_T$ relative to the values determined for **6** and **7**. Thus, the minimum-energy conformers of **14** (*Fig. 1, c*; $E_S = 48.4$ kcal/mol, $E_T = 58.5$ kcal/mol) and **15** (*Fig. 1, d*; $E_S = 47.9$ kcal/mol, $E_T = 58.0$ kcal/mol) exhibit strain and total energy levels that modestly favor **15**.

To test these conclusions, **13** was oxidized with PDC to produce **14** (96%, *Scheme 3*). For **12**, the strategically important $\beta$-(*t*-Bu)$Me_2$Si substituent causes the 'carbonyl down' atropisomer to be thermodynamically favored [1b]. This topography persists as expected in **13** and is not relaxed in **14**[2]). Both compounds feature *inter alia* a deshielded vinyl proton (5.43 and 5.44 ppm, respectively, in $CDCl_3$) indicating it to be positioned well away from the flank of the transannular C=O group [1b].

The thermodynamic driving force for conversion to **15** has indeed proven adequate to be highly utilitarian. Thus, treatment of **14** with MeONa in hot MeOH established a 1:1 equilibrium with the desired *trans*-diastereoisomer **15** (5.47 ppm). Following chromatographic separation, unchanged **14** can be recycled to achieve a throughput efficiency of *ca.* 80%.

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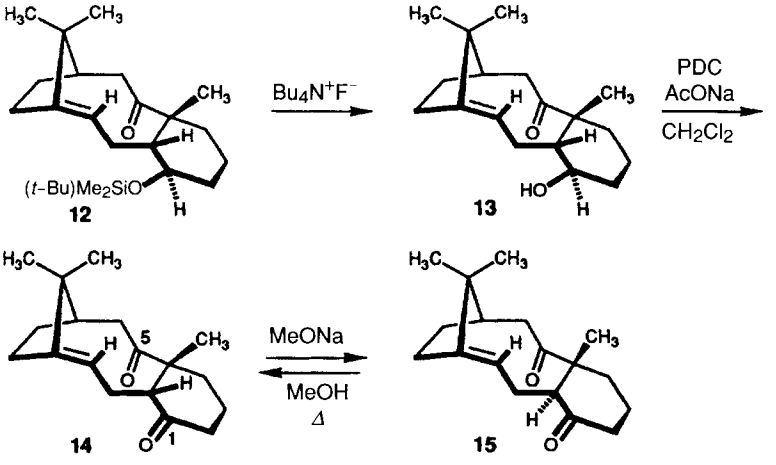
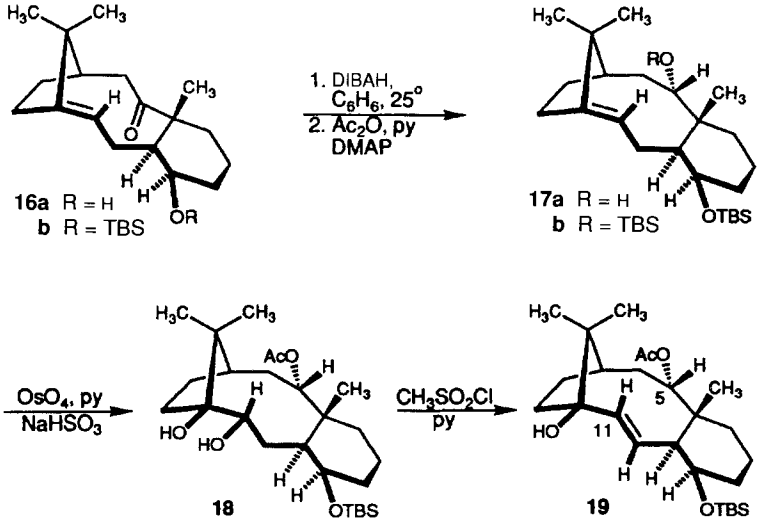
[2]) While experimental evidence indicates **14** to be the 'carbonyl down' atropisomer, MMX calculations suggest the 'carbonyl up' geometry to be more favorable by a $\Delta E_T$ of 0.8 kcal/mol. The possible thermal equilibration of **14** has not been investigated.

*Scheme 3*




*Influence of* trans-*B*/*C*-*Configuration on the Course of Pinacol-Like* Wagner-Meerwein *Shifts.* Our willingness to consider **15** as a pivotal intermediate was facilitated by the knowledge that this diketone is conformationally inflexible at ordinary temperatures, and that the disparate steric shielding of the two C=O groups can lead to selective reduction in a completely regio- and stereoselective manner. While DIBAH (diisobutylaluminum hydride) in *benzene* is too reactive to be discriminating, use of this reducing agent in *THF* results in quantitative conversion to **16a** (*Scheme 4*).

*Scheme 4*




TBS = (*t*-Bu)$Me_2$Si; DMAP = 4-(dimethylamino)pyridine.

Once silylation to give **16b** had been accomplished, recourse to DIBAH in *benzene* made possible the efficient conversion to 5α-alcohol **17a**. NOE studies indicated that a conformational realignment occurs in **17a** to enable the OH group to be oriented pseudoequatorially. MM2 calculations on the parent diol agree that this global minimum is adopted (*Fig. 2, a*), the issue being critical to achieving proper bond alignments in the projected rearrangements.

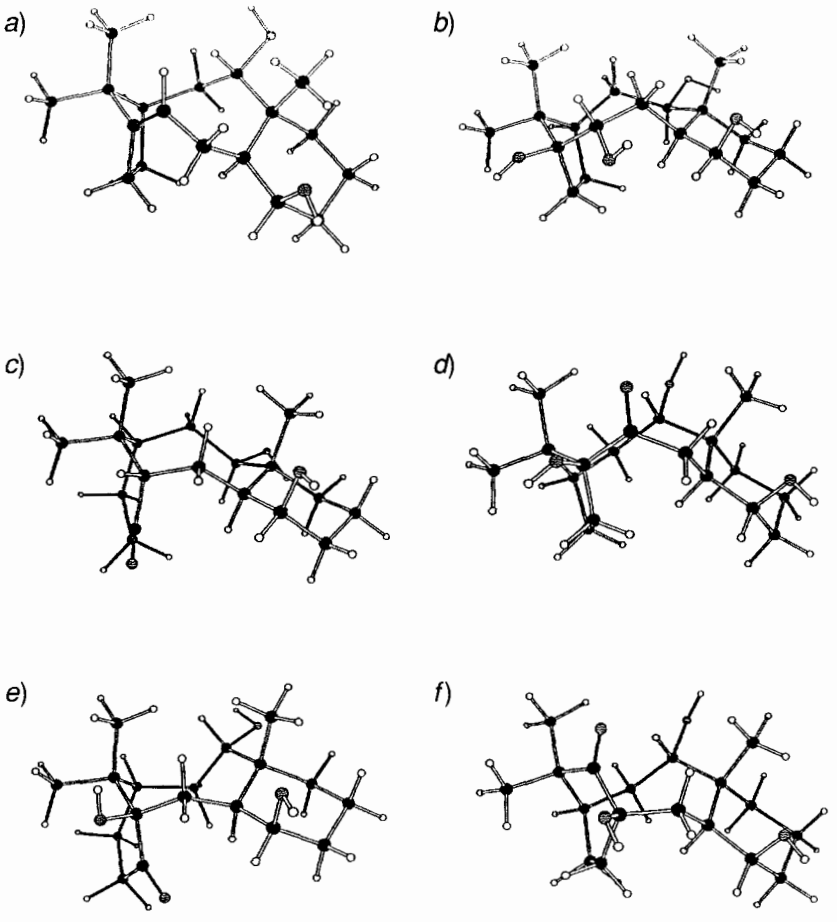


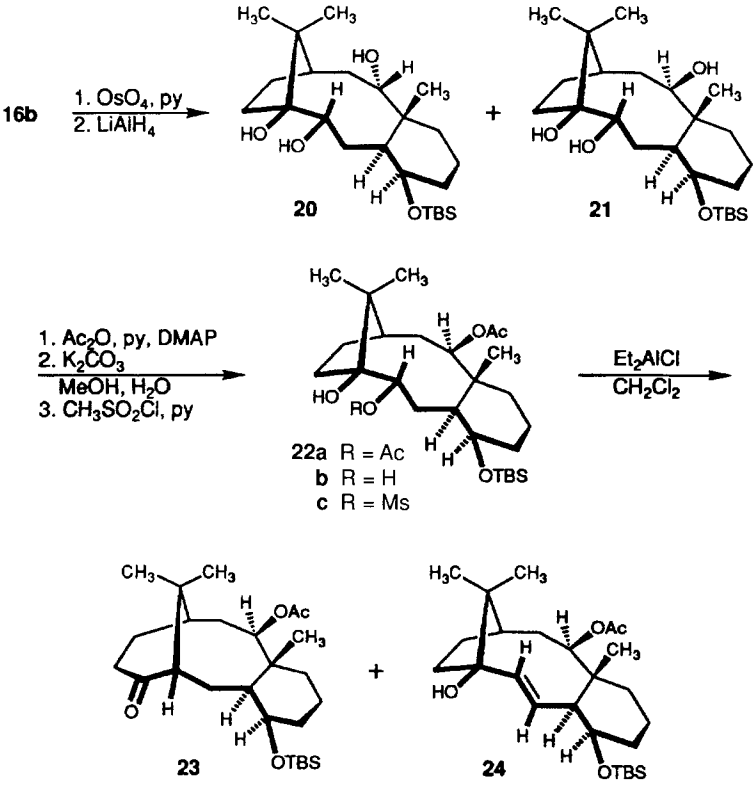

Fig. 2. *Global-minimum-energy conformations of* a) *the diol corresponding to* **17**; b) *the parent tetrol of* **22**; c) *the dihydroxy ketone corresponding to* **23**; d) *the parent trihydroxy ketone of* **27**; e) *the trihydroxy ketone corresponding to* **28**; *and* f) *the trihydroxy ketone related to* **29** (Chem 3-D output). The silyl groups have been omitted to simplify matters.

With the structure and configuration of **17a** and its acetate **17b** secure, the (*E*)-configurated C=C bond was osmylated to furnish diol **18**. Rather unexpectedly, diol **18** failed to give any trace of pinacol product [7] when treated with MsCl in pyridine. Instead, simple $E_2$ elimination occurred during workup to give **19** in 88% yield. To all appearances, this

facile loss of MsOH does not derive from a structurally induced misalignment of antiperiplanarity, but stems from a most suitably positioned $\beta$-C–H bond.

A logical outgrowth of this hypothesis is the need to alter the conformation of the central ring judiciously. Partial success was realized by osmylation of **16b** followed directly by $LiAlH_4$ reduction (*Scheme 5*). In this instance, the osmate ester appears to have lost rigidity within the nine-membered ring, since the epimeric tirols **20** and **21** are produced in equal amounts.

*Scheme 5*




TBS = (*t*-Bu)$Me_2$Si; DMAP = 4-(dimethylamino)pyridine.

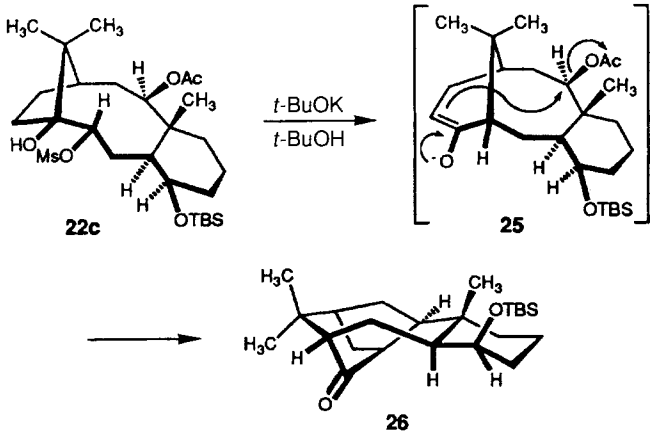
Conversion of **21** to diacetate **22a** permitted subsequent selective hydrolysis to give **22b**. The $\beta$-orientation of the AcO group in this intermediate so affects the *trans*-tricyclo[10.2.1.$0^{4,9}$]pentadecane framework that the mesylate derivative is now isolable and stable. As a first experiment, **22c** was treated with $Et_2AlCl$ in $CH_2Cl_2$ at −78° to +25°. These conditions promoted closely comparable levels of pinacolization and elimination[3]). The configurations of the *trans*-cyclononene rings in both **19** and **24** were defined by the

[3]) Under identical conditions, (i-PrO)$_2$TiCl gave a 3:5 mixture of **20**/**21**.

large coupling constants between their vinyl protons ($J$ = 12.2 and 13.5 Hz, respectively) and the significant NOE interactions involving the *syn*-apical Me group and H–C(11). In **19**, the $\beta$-orientation of H–C(5) was also reconfirmed during these experiments.

The less than complete isomerization of **22c** to **23** does not appear to arise from untoward thermodynamic factors. In actuality, MM2 calculations comparing the minimum total energy of the parent tetrol of **22** (*Fig. 2, b*) with that of the dihydroxy ketone corresponding to **23** (*Fig. 2, c*) show the latter to be more stable by 10.3 kcal/mol! For these reasons, additional attempts were made to curtail competitive elimination with **22c** through utilization of strongly basic conditions for achieving the *Wagner-Meerwein* shift. As seen in *Scheme 6*, the use of *t*-BuOK in *t*-BuOH is indeed conductive to the migration of C(13). However, ketone **23** so formed appears to enolize readily under these conditions. Once **25** is produced, intramolecular $S_N2$ displacement of acetate ion occurs to deliver tetracyclic ketone **26**. Deterrence of this C–C bond-forming reaction might be realized by positioning a poorer leaving group at C(15). Under these circumstances, direct conversion to *trans*-tricyclo[9.3.1.$0^{3,8}$]pentadecan-14-ones could beome a serviceable entry to taxusin.

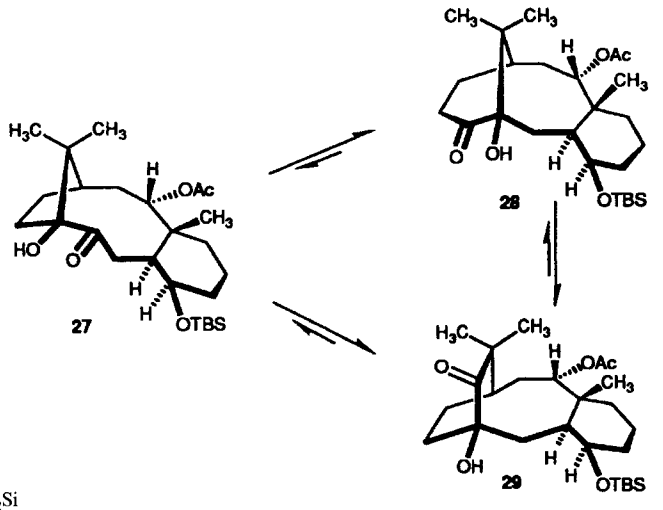
*Scheme 6*




TBS = (*t*-Bu)$Me_2$Si

*The α-Hydroxy-Ketone Rearrangement.* Following *Swern* oxidation of **18** to **27**, the stage was set for examining the capability of this α-hydroxy ketone for interconversion with its structural isomers **28** and **29** (*Scheme 7*). The hope at the outset was that the isomerization would be directed preferentially to **28** if performed under neutral conditions [8]. This expectation was fueled by MM2 calculations showing the global-minimum-energy geometry of **27** (*Fig. 2, d*) to reside in the 'carbonyl-up' conformer. As a consequence, C(13) is uniquely aligned stereoelectronically with the C=O $\pi$ cloud for directed operation of the *Wagner-Meerwein* shift. However, the energetics of the situation as determined computationally projects **28** (*Fig. 2, e*) as being modestly more strained (by *ca.* 0.75 kcal/mol) than **27**. This trend is exactly opposite to that uncovered for the *cis*-B/C-analogues [1e].

*Scheme 7*




TBS = (*t*-Bu)$Me_2$Si

When **27** did not respond to thermal activation, attention was turned to catalysis by aluminum reagents as a direct outgrowth of our earlier successes [1e]. This selection is not without conformational consequences, as coordination of the Al-atom to the neighboring O-centers in **27** would surely alter the relative geometry of the C=O group perhaps so as to favor **29**. This eventuality could prove to be less than ideal, since **29** was calculated to be the thermodynamic sink of the triad. In its most favorable geometry (*Fig. 2,f*), **29** is calculated to be 2.8 kcal/mol more stable than **27**.

At the experimental level, heating **27** with either (i-PrO)$_3$Al or (*t*-BuO)$_3$Al in benzene at 50° for 1 h resulted in the partial conversion of **27** to both **28** and **29** (ratio 17:42:38, 96% mass recovery). When the reaction temperature was raised to the reflux point of the solvent and the equilibration prolonged to 3 h, **27** was no longer present in the mixture, which was now constituted of 15% of **28** and 85% of **29**. Further extension of the reaction time to 12 h resulted in clean conversion only to **29** (93% isolated). Consequently, although quantitites of **28** could be isolated from the short-term experiments, the thermodynamics associated with this triad of isomers favor **29** sufficiently to allow it to dominate completely.

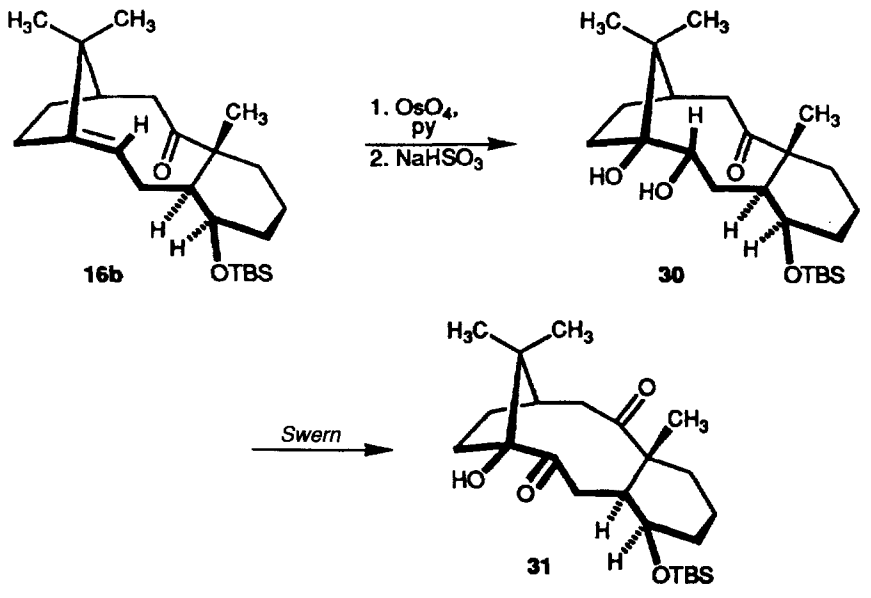
$^1$*H*-NMR analysis of **28** indicated it to be a mixture of two or more conformational isomers at room temperature. Gradual warming of $C_6D_5Br$ solutions containing **28** in the probe of a 300-MHz spectrometer induced coalescence of the original very broad signals and ultimately led at 420 K to a clearly defined, sharp spectrum. The structural features of **29** were corroborated by selective DEPT-enhancement studies involving the irradiation of selected $^1$H signals with concurrent observation of $^{13}$C absorptions[4]).

The complications discussed above were conveniently skirted by transforming **16b** to **31** as shown in *Scheme 8*. Cleavage of the osmate ester could be accomplished efficiently

[4]) We thank Dr. *Dirk Friedrich* for these experiments.

either with $NaHSO_3$ or with $LiAlH_4$. Importantly, dihydroxy ketone **30** is *not* subject to transannular hemiketalization, a process that cannot be impeded in the *cis*-B/C-series [1c]. Arrival at **31** was accomplished through use of typical *Swern* conditions.

*Scheme 8*

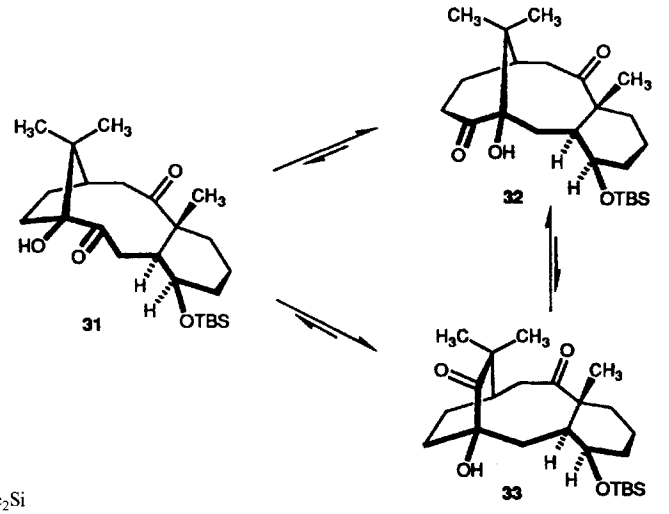



TBS = (*t*-Bu)$Me_2$Si

Evaluation of the global-energy minima determined for **31** and its isomers **32** and **33** (*Scheme 9*) by means of molecular mechanics (*Fig. 3*) indicated both **31** ($E_S = 47.5$ kcal/mol, $E_T = 62.4$ kcal/mol) and **33** ($E_S = 44.4$ kcal/mol, $E_T = 60.2$ kcal/mol) to be *more strained* than the *trans*-tricyclo[9.3.1.$0^{3,8}$]pentadecane **32** ($E_S = 41.4$ kcal/mol, $E_T = 56.3$ kcal/mol). In line with these results, **31** was found to be completely consumed when stirred with 3 equiv. of (*t*-BuO)$_3$Al in benzene at 25° for 4 h. Chromatography of the resulting two-component mixture resulted in the isolation of **32** (54%) and **33** (35%). The equilibration is much slower in THF. After 12 h at 25°, the distribution of **31**/**32**/**33** had advanced only to the 17:46:37 level ($^1$H-NMR analysis). In preparative experiments, **31** has simply been heated in benzene with the catalyst for 12 h. The conditions are conveniently conductive to the isolation of **32** in 87% yield. This hydroxy diketone is characterized by very sharp $^1$H-NMR signals at room temperature, thereby indicating it to reside in a reasonably fixed conformation at room temperature. It is, in fact, likely that this conformation closely resembles that illustrated in *Fig. 3, b*.

**Discussion.** – The efficient coupling of funtionalized cyclohexenyl cerates to (*R*)-7,7-dimethyl-1-vinylbicyclo[2.2.1]heptan-2-one as a means of gaining ready access to **1** has previously been described [1a,b,d]. The remarkable success of the ensuing anionic oxy-*Cope* rearrangement of these alcohols has been detailed. Quite aside from the fact that a single transition-state geometry is adopted (four options are available) [1a], enolate

*Scheme 9*




TBS = (*t*-Bu)$Me_2Si$

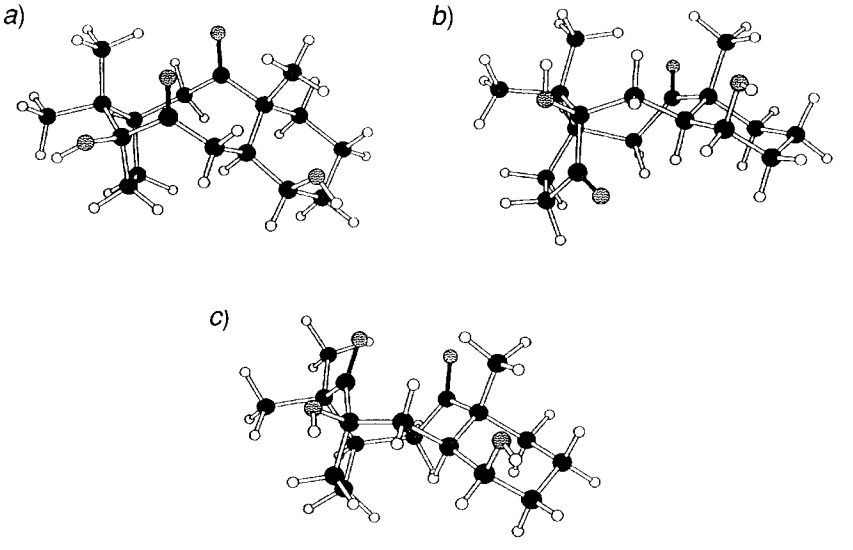



Fig. 3. *Global-minimum-energy conformations of the hydroxy diketones* a) **31**, b) **32**, *and* c) **33** (Chem 3-D output). The silyl groups have been omitted to simplify matters.

anions are generated that have proven amenable to direct *in situ* methylation. The value of this new chemistry is to make tricyclic ketones such as **2** and **2′** available in two laboratory operations.

It now appears from the present and related studies [1c,e] that 1,2-migration of the *gem*-dimethyl substituted bridge in these molecules is a most powerful and convenient method for constructing the tricyclo[9.3.1.$0^{3,8}$]pentadecane ring system common to the

taxane diterpenes [3] in the proper absolute configuration. Furthermore, the developed chemistry accommodates for the first time the broadly defined goals of producing serviceable precursors to both taxusin (bridgehead H) and taxol (bridgehead OH) on demand. Consequently, this technology has been placed high on our list of choices as the operational paradigm that will hopefully eventuate in efficient total syntheses of these important target molecules.

With the initial focus on producing an advanced intermediate capable of being utilized in either direction, the oxy-*Cope* product **12** was transformed in five steps to **16b**. Molecular modeling was found to be very useful in guiding these studies and subsequent transformations. Of the many chemo- and regioselective reactions developed in the course of this work, the controlled reduction of **15** to **16a** with DIBAH in THF ranks as one of the more significant.

With **16b** as the point of bifurcation, the sequence to **23** was engineered to take advantage of stereospecific osmylation, selective hydrolysis of the derived diacetate, and pinacol-like bridge migration within mesylate **22c** as catalyzed by $Et_2AlCl$. Subtle conformational interactions are recognized to play an important role in establishing the antiperiplanar geometry so necessary to the successful operation of the desired 1,2-shift. This direct solution to construction of a potential taxusin precursor, which requires only 12 steps, has been engineered to possess flexibility, thereby possibly opening the way to structural modifications that could lead equally well to related bridgehead non-oxygenated taxanes such as taxinine [9], baccatin I [10], and taxagifine [11].

Still more abbreviated (10 steps) is the route that leads to **32**. With much of the necessary functionality and proper configuration installed, **32** represents the most advanced taxol-like compound to be reported to date. The implications of its successful preparation extend far beyond its acquisition by the present scheme. For example, studies now in progress are being directed to amplification of the level of oxygenation, to preinstallation of the oxetane subunit, and to other structural modifications that could eventuate as well in the successful total synthesis of deacetylbaccatin III [12] and cephalomannine [13] in addition to taxol.

We thank the *National Institutes of Health* (grant CA-12115) and *Bristol Myers Squibb* for financial support, *Dirk Friedrich* for NMR measurements, *Eugene Hickey* for the molecular-mechanics calculations, and *Kurt Loening* for assistance with the nomenclature.

## Experimental Part

*General.* M.p.: uncorrected. Solvents: reagent grade and in most cases dried prior to use. The column chromatographic separations: performed with *Woelm* silica gel (230–400 mesh). The purity of all compounds was shown to be $\geq 95\%$ by TLC and high-field $^1$H-NMR analyses. $^1$H-NMR spectra: at 300 MHz; $^{13}$C-NMR spectra: at 75 MHz unless otherwise noted. HR- and FAB-MS: obtained at The Ohio State University Campus Chemical Instrumentation Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

*(1S,4aR,5R,7R,10E,12aR)-1,2,3,4,4a,5,6,7,8,9,12,12a-Dodecahydro-4a,13,13-trimethyl-7,10-methanobenzocyclodecene-1,5-diol* (**5b**). A soln. of **5a** [1e] (50 mg, 0.13 mmol) in dry THF (5 ml) was treated with 0.64 ml of 1.0M $Bu_4N^+F^-$ in THF (0.64 mmol), refluxed overnight under $N_2$, diluted with $Et_2O$ (40 ml), and washed with $H_2O$ (10 ml) and brine (10 ml). The aq. layers were extracted with $Et_2O$ (2 × 20 ml) and the combined $Et_2O$ solns. were dried

and concentrated to leave a residue that was purified chromatographically (elution with 30% AcOEt in petroleum ether): 28.5 mg (79%) of **5b**. Colorless solid. M.p. 195–196°. $[\alpha]_D^{21} = -76.1$ ($c = 0.71$, $CHCl_3$). IR ($CHCl_3$): 3610. $^1$H-NMR ($CDCl_3$): 4.90 (*d*, $J = 11.4$, 1 H); 3.95 (*dt*, $J = 12.2$, 4.1, 1 H); 3.14 (*d*, $J = 6.2$, 1 H); 2.30 (*dd*, $J = 3.1$, 13.3, 1 H); 2.22–2.00 (*m*, 1 H); 2.00–1.85 (*m*, 3 H); 1.80–1.60 (*m*, 1 H); 1.60–1.25 (*m*, 10 H); 1.25–1.05 (*m*, 1 H); 1.15 (*s*, 3 H); 1.05 (*s*, 3 H); 1.05–0.90 (*m*, 1 H); 0.90 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 142.2; 124.9; 75.9; 70.0; 54.0; 46.9; 42.7; 31.9; 30.64; 30.56; 26.2; 25.0; 23.0; 21.7; 20.5 (2 C); 16.1 (1 C not observed). MS: $M^+$ calc.: 278.2246; observed: 278.2218. Anal. calc. for $C_{18}H_{30}O_2$: C 77.65, H 10.86; found: C 77.76, H 10.82.

*(4a*R,*5*R,*7*R,*10*E,*12a*S*)-2,3,4,4a,6,7,8,9,12,12a-Decahydro-5-hydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-1(1*H*)-one* (**6**). To a soln. of **5b** (31 mg, 0.11 mmol) in $CH_2Cl_2$ (2 ml) containing AcONa (5 mg, 0.055 mmol) was added pyridinium dichromate (68 mg, 0.18 mmol). The mixture was stirred at r.t. for 3 h, diluted with $Et_2O$ (50 ml), and filtered through *Celite*. The filter cake was rinsed with $Et_2O$ (50 ml), and the combined filtrates were concentrated to give 30.3 mg (99%) of **6** as a white solid. M.p. 148–150°. $[\alpha]_D^{21} = -91.1$ ($c = 0.88$, $CHCl_3$). IR ($CHCl_3$): 3608, 1695. $^1$H-NMR ($CDCl_3$): 4.95 (*d*, $J = 11.3$, 1 H); 3.24 (*d*, $J = 6.1$, 1 H); 2.56–2.46 (*m*, 1 H); 2.46–2.12 (*m*, 5 H); 2.12–1.50 (*m*, 9 H); 1.41 (*d*, $J = 15.8$, 1 H); 1.40–1.00 (*m*, 1 H); 1.14 (*s*, 3 H); 1.02 (*s*, 3 H); 0.80 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 214.2; 144.0; 122.0; 74.7; 63.5; 46.9; 44.9; 42.3; 38.6; 32.3; 30.7; 28.0; 26.0; 24.8; 23.1; 20.3; 16.7. MS: $M^+$ calc.: 276.2090; observed: 276.2085. Anal. calc. for $C_{18}H_{28}O_2$: C 78.21, H 10.21; found: C 77.81, H 10.26.

*(4a*R,*5*R,*7*R,*10*E,*12a*S*)-2,3,4,4a,6,7,8,9,12,12a-Decahydro-5-hydroxy-4a,13,13-trimethyl-1-oxo-7,10-methano-1*H*-benzocyclodecen-5-yl Acetate* (**8**). A soln. of **6** (163 mg, 0.59 mmol) in $CH_2Cl_2$ (15 ml) was treated at 0° with pyridine (0.3 ml, 3.54 mmol) and AcCl (0.21 ml, 2.95 mmol). The mixture was poured into sat. $NaHCO_3$ soln. (50 ml), and the aq. layer was extracted with $Et_2O$ (3 × 20 ml). The combined org. phases were washed with brine (50 ml), dried, and concentrated. The residue was chromatographed (elution with 10% AcOEt in petroleum ether) to give **8** (124 mg, 66%) as a white solid. M.p. 160–165°. $[\alpha]_D^{21} = -116$ ($c = 0.67$, $CHCl_3$). IR ($CHCl_3$): 1725, 1702. $^1$H-NMR ($CDCl_3$): 4.93 (*d*, $J = 11.0$, 1 H); 4.84 (*d*, $J = 4.0$, 1 H); 2.68–2.51 (*m*, 1 H); 2.48–2.30 (*m*, 1 H); 2.30–2.10 (*m*, 3 H); 2.01 (*s*, 3 H); 2.00–1.65 (*m*, 3 H); 1.61–1.56 (*m*, 1 H); 1.51–1.17 (series of *m*, 7 H); 1.10 (*s*, 3 H); 1.01 (*s*, 3 H); 0.81 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 213.3; 170.5; 144.2; 122.0; 77.5; 63.9; 47.3; 45.3; 42.8; 38.3; 29.2; 28.2; 25.5; 24.6; 23.2; 21.4; 21.1; 20.6; 17.6. MS: $M^+$ calc.: 318.2195; observed: 318.2163. Anal. calc. for $C_{20}H_{30}O_3$: C 75.43, H 9.4; found: C 75.08, H 9.51.

*$NaBH_4$-Promoted Reduction of* **8**. To a soln. of **8** (80 mg, 0.239 mmol) in EtOH (10 ml) was added $NaBH_4$ (18 mg, 0.48 mmol) at r.t. The mixture was stirred for 1 h, at which point another 18 mg of $NaBH_4$ was introduced. After 1 h, the solvent was removed *in vacuo*, and the residue was treated with $H_2O$ (10 ml) and extracted with $Et_2O$ (3 × 10 ml). The combined org. phases were dried and evaporated. Chromatography of the remaining oil on silica gel (elution with hexane/AcOEt 4:1) gave 58 mg (72%) of **9a** and 23 mg (28%) of **9b**.

*Data of* **9a**: white solid. M.p. 127–130°. $^1$H-NMR ($CDCl_3$): 4.98 (br. *d*, $J = 11.5$, 1 H); 4.68 (*d*, $J = 5.7$, 1 H); 4.03 (br. *s*, 1 H); 2.54–2.41 (*m*, 2 H); 2.16–2.08 (*m*, 1 H); 2.02 (*s*, 3 H); 1.96–1.81 (*m*, 1 H); 1.76–1.16 (series of *m*, 13 H); 1.13 (*s*, 3 H); 1.12 (*s*, 3 H); 1.06 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 170.8; 142.8; 123.8; 79.5; 75.0; 53.5; 47.3; 43.0; 40.7; 31.4; 29.8; 29.7; 28.7; 25.7; 24.7; 23.3; 21.6; 20.6; 18.4; 15.8. FAB-MS: $M^+$ calc.: 320.24; observed: 320.28.

*Data of* **9b**: colorless oil. $^1$H-NMR ($CDCl_3$): 4.89 (br. *d*, $J = 11.2$, 1 H); 4.74 (*d*, $J = 5.4$, 1 H); 3.88 (*td*, $J = 4.2$, 12.1, 1 H); 2.53–2.43 (*m*, 1 H); 2.30 (*dd*, $J = 3.0$, 13.2, 1 H); 2.18–2.07 (*m*, 2 H); 1.99 (*s*, 3 H); 1.94–1.80 (*m*, 2 H); 1.61–1.14 (series of *m*, 11 H); 1.10 (*s*, 3 H); 1.03 (*s*, 3 H); 0.90 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 170.6; 142.2; 125.0; 79.2; 69.6; 54.4; 47.2; 43.4; 43.3; 30.5; 30.4; 29.2; 25.7; 24.7; 23.1; 22.0; 21.5; 20.7; 20.2; 16.8. FAB-MS: $M^+$ calc.: 320.24; observed: 320.31.

O-*Silylation of* **9a** *and* **9b**. A soln. of either **9a** or **9b** (20 mg, 0.062 mmol) in $CH_2Cl_2$ (3 ml) was treated sequentially with $Et_3N$ (25 µl, 0.18 mmol) and (*tert*-butyl)dimethylsilyl triflate (30 µl, 0.13 mmol) at 0–5°. The mixture was stirred for 1 h, quenched with $H_2O$ (10 ml), and extracted with $Et_2O$ (2 × 10 ml). The combined org. extracts were dried and evaporated to leave a yellow oil, which was purified by silica-gel chromatography (elution with hexane/AcOEt 25:1): 21 mg (78%) of **10a** or **10b**.

*Data of* **10a**: colorless oil. $[\alpha]_D^{20} = -37.2$ ($c = 1.75$, $CHCl_3$). IR (neat): 1732, 1260. $^1$H-NMR ($CDCl_3$): 4.92 (br. *d*, $J = 11.6$, 1 H); 4.65 (*d*, $J = 5.5$, 1 H); 3.89 (br. *d*, $J = 2.7$, 1 H); 2.51–2.37 (*m*, 2 H); 2.16–2.06 (*m*, 1 H); 2.01 (*s*, 3 H); 1.94–1.77 (*m*, 2 H); 1.76–1.69 (*m*, 1 H); 1.63–1.23 (*m*, 10 H); 1.12 (*s*, 3 H); 1.08 (*s*, 3 H); 1.05 (*s*, 3 H); 0.90 (*s*, 9 H); 0.07 (*s*, 3 H); 0.04 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 170.8; 142.5; 123.9; 79.7; 75.2; 53.9; 47.1; 43.0; 40.8; 31.5; 29.9; 29.6; 29.2; 25.9; 25.7; 24.7; 23.2; 21.6; 20.6; 18.5; 18.1; 16.0; –4.9; –5.1. MS: $M^+$ calc.: 434.3216; observed: 434.3228. Anal. calc. for $C_{26}H_{46}O_3Si$: C 71.83, H 10.66; found: C 71.46, H 10.70.

*Data of* **10b**: colorless solid. M.p. 142–144°. $[\alpha]_D^{20} = -99.6$ ($c = 0.83$, $CHCl_3$). IR ($CHCl_3$): 1723, 1260. $^1$H-NMR ($CDCl_3$): 4.87 (br. *d*, $J = 11.3$, 1 H); 4.75 (*d*, $J = 5.4$, 1 H); 3.82 (*td*, $J = 4.4$, 15.6, 1 H); 2.56–2.46 (*m*, 2 H); 2.18–2.03 (*m*, 2 H); 2.01 (*s*, 3 H); 1.95–1.83 (*m*, 1 H); 1.61–1.15 (series of *m*, 11 H); 1.12 (*s*, 3 H); 1.05 (*s*, 3 H);

0.91 (*s*, 3 H); 0.89 (*s*, 9 H); 0.06 (*s*, 3 H); 0.05 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 170.6; 141.8; 125.5; 79.3; 70.1; 55.4; 47.1; 43.40; 43.35; 31.1; 30.5; 29.2; 25.8; 25.7; 24.7; 23.1; 22.1; 21.5; 20.7; 20.3; 18.1; 17.0; –4.5; –4.7. MS: $M^+$ calc.: 434.3216; observed: 434.3209. Anal. calc. for $C_{26}H_{46}O_3Si$: C 71.83, H 10.66; found: C 71.94, H 10.73.

*Acetylation of* **5a**. A soln. of **5a** (100 mg, 0.255 mmol) in $CH_2Cl_2$ (10 ml) was treated with pyridine (121 mg, 1.53 mmol) and AcCl (100 mg, 1.28 mmol) at 0°. The mixture was stirred overnight at this temp., allowed to warm to r.t., and quenched with sat. $NH_4Cl$ soln. (10 ml). The org. phase was washed with $H_2O$ (5 ml) and sat. $NaHCO_3$ and NaCl solns. Drying and chromatography of the residue on silica gel (elution with hexane/AcOEt 20:1) afforded 90 mg (81%) of a white solid. M.p. 142–144°, identical in all respects with **10b**.

*(1S,4aR,5R,10S,11S,12aR)-1-[(*tert*-Butyl)dimethylsilyloxy]perhydro-10,11-dihydroxy-4a,13,13-trimethyl-7,10-methano-2H-benzocyclodecen-5-yl Acetate* (**11**). To a soln. of **10b** (83 mg, 0.19 mmol) in $CH_2Cl_2$ (12 ml) was added a soln. of $OsO_4$ (0.61 ml, 120 mg/ml, 0.29 mmol) in $CH_2Cl_2$ at r.t. After 1.5 h of stirring, the solvent was removed *in vacuo*, and the black residue was treated with EtOH (10 ml) and $NaBH_4$ (43 mg, 1.15 mmol). After 1.5 h, and additional 43 mg of $NaBH_4$ was introduced, stirring was maintained for 1 h, and the solvent was evaporated. $H_2O$ (5 ml) and $Et_2O$ (10 ml) were added, and the aq. phase was extracted with $Et_2O$ (2 × 10 ml). The combined org. layers were dried and evaporated, and the residue was chromatographed (elution with 20% AcOEt in hexane) to give **11** (65 mg, 78%) as a mixture of two atropisomers. White foam. M.p. 60°. IR (neat): 3600–3200, 1732, 1462. $^1$H-NMR ($CDCl_3$): 5.10–5.05 (*m*, 1 H); 4.18–3.64 (*m*, 2 H); 2.66–1.20 (series of *m*, 18 H); 2.02, 1.99 (*s*, 3 H); 1.15, 1.12 (*s*, 3 H); 1.06, 1.05 (*s*, 3 H); 0.99, 0.94 (*s*, 3 H); 0.90, 0.89 (*s*, 9 H); 0.79, 0.52 (*s*, 6 H). $^{13}$C-NMR ($CDCl_3$): 170.6; 170.4; 94.7; 86.0; 85.1; 77.3; 77.2; 76.9; 76.0; 70.5; 69.6; 47.9; 47.3; 45.8; 45.0; 44.4; 42.9; 41.8; 41.4; 32.5; 32.3; 31.9; 30.9; 30.4; 29.5; 29.4; 29.3; 28.8; 28.7; 27.9; 25.9; 25.7; 25.2; 22.9; 21.8; 21.3; 20.0; 20.0; 19.7; 19.5; 18.2; 18.0; 16.9; 16.2; –4.5; –4.67; –4.70; –4.8. MS: $M^+$ calc.: 468.3271; observed: 468.3272.

*(1R,4aR,7R,10E,12aR)-2,3,4,4a,6,7,8,9,12,12a-Dodecahydro-1-hydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5(1H)-one* (**13**). A soln. of **12** [1b] (107 mg, 0.274 mmol) in dry THF (5 ml) together with 1.68 ml of 1.0M $Bu_4N^+F^-$ in THF (1.68 mmol) was refluxed overnight under $N_2$, diluted with $H_2O$ (10 ml), and washed with $H_2O$ (10 ml) and brine (10 ml). The org. phase was dried and concentrated to leave a residue that was purified chromatographically (elution with 30% AcOEt in petroleum ether): 76 mg (100%) of **13**. Colorless solid. M.p. 116–117° (from $Et_2O$). $[\alpha]_D^{19} = -287$ ($c = 0.15$, $CHCl_3$). IR ($CHCl_3$): 3620, 1668. $^1$H-NMR ($CDCl_3$): 5.43 (*dd*, $J = 4.4$, 12.8, 1 H); 3.91 (*m*, 1 H); 2.63 (*d*, $J = 12.9$, 1 H); 2.52 (*m*, 1 H); 2.22 (*t*, $J = 9.1$, 1 H); 2.18–1.78 (series of *m*, 8 H); 1.68–1.52 (*m*, 1 H); 1.49–1.43 (*m*, 2 H); 1.41 (*s*, 3 H); 1.39–1.35 (*m*, 1 H); 1.22 (*s*, 3 H); 1.16–1.06 (*m*, 2 H); 1.09 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 214.2; 147.3; 121.0; 76.4; 56.8; 51.4; 51.1; 45.1; 39.2; 36.1; 34.8; 31.8; 30.2; 25.7; 24.5; 21.9; 20.9; 20.0. MS: $M^+$ calc.: 276.2089; observed: 276.2116. Anal. calc. for $C_{18}H_{28}O_2$: C 78.21, H 10.21; found: C 77.82, H 10.24.

*(4aR,7R,10E,12aR)-2,3,4,4a,6,7,8,9,12,12a-Decahydro-4a,13,13-trimethyl-7,10-methanobenzocyclodecene-1,5-dione* (**14**). To a soln. of pyridinium dichromate (87 mg, 0.231 mmol) and AcONa (6 mg, 0.074 mmol) in $CH_2Cl_2$ (2 ml) was added a soln. of **13** (38 mg, 0.138 mmol), and the mixture was stirred at 25° for 3 h, diluted with $Et_2O$ (20 ml), and filtered through *Celite*/silica gel 1:1. The filter cake was rinsed with $Et_2O$ (50 ml) and the filtrate evaporated to give 37 mg (97%) of **14** after chromatography (elution with 20% AcOEt in petroleum ether). M.p. 95–97°. $[\alpha]_D^{20} = -104$ ($c = 0.52$, $CHCl_3$). IR ($CHCl_3$): 1701, 1665. $^1$H-NMR ($CDCl_3$): 5.44 (*dd*, $J = 5.2$, 12.5, 1 H); 3.02 (*ddd*, $J = 6.6$, 12.6, 14.2, 1 H); 2.64 (*d*, $J = 12.7$, 1 H); 2.45 (*dt*, $J = 15.2$, 4.7, 1 H); 2.34 (*dd*, $J = 6.5$, 9.2, 1 H); 2.20–2.04 (*m*, 2 H); 1.98–1.61 (*m*, 9 H); 1.58 (*s*, 3 H); 1.53 (*dd*, $J = 6.1$, 12.9, 1 H); 1.20 (*s*, 3 H); 1.09 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 211.8; 209.5; 148.7; 120.2; 60.3; 55.5; 51.4; 45.0; 39.8; 38.6; 35.3; 29.0; 25.6; 24.6; 22.2; 21.8; 20.9; 20.9. MS: $M^+$ calc.: 274.1933; observed: 274.1929. Anal. calc. for $C_{18}H_{26}O_2$: C 78.79, H 9.55; found: C 78.62, H 9.50.

*(4aR,7R,10E,12aS)-2,3,4,4a,6,7,8,9,12,12a-Decahydro-4a,13,13-trimethyl-7,10-methanobenzocyclodecene-1,5-dione* (**15**). A soln. of **14** (1.09 g, 3.65 mmol) in MeOH (20 ml) containing MeONa (1.0 ml of 0.5M in MeOH, 0.5 mmol) was heated at reflux for 2 d, diluted with AcOEt (100 ml) and washed with $H_2O$ (3 × 50 ml). The org. phase was dried and concentrated. The residue was chromatographed (elution with 8% AcOEt in petroleum ether) to return 556 mg (54%) of **14** and furnish 388 mg (36%) of **15**. Repetition of this procedure with the recovered **14** gave 375 mg (50%) of **14** and 248 mg (45%) of **15**. One additional pass with this lot of **14** afforded 148 mg (54%) of **14** and 107 mg (39%) of **15**.

*Data of* **15**: white solid. M.p. 103–104°. $[\alpha]_D^{21} = +43.5$ ($c = 0.405$, $CHCl_3$). IR ($CHCl_3$): 1701, 1663. $^1$H-NMR ($CDCl_3$): 5.47 (*dd*, $J = 7.1$, 11.2, 1 H); 3.56 (*dd*, $J = 4.1$, 10.7, 1 H); 2.90–2.81 (*m*, 1 H); 2.74 (*d*, $J = 12.8$, 1 H); 2.44–2.30 (*m*, 3 H); 2.27–1.71 (series of *m*, 8 H); 1.64–1.43 (*m*, 2 H); 1.28 (*s*, 3 H); 1.22 (*s*, 3 H); 1.10 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 214.5; 211.9; 147.8; 121.0; 58.9; 56.6; 51.3; 44.8; 41.5; 40.3; 35.0; 25.6; 24.4; 22.9; 22.0; 21.2; 19.5; 19.4. MS: $M^+$ calc.: 274.1933; observed: 274.1914. Anal. calc. for $C_{18}H_{26}O_2$: C 78.79, H 9.55; found: C 78.90, H 9.59.

*(1R,4aR,7R,10E,12aS)-2,3,4,4a,6,7,8,9,12,12a-Decahydro-1-hydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5(1H)-one* (**16a**). A cold (−78°) soln. of **15** (233 mg, 2.68 mmol) in anh. THF (10 ml) was treated with 2.94 ml of 1.0M DIBAH in hexane (2.94 mmol), stirred at −78° for 1 h, and quenched with MeOH (2 ml). Following the addition of sat. sodium potassium tartrate soln. (10 ml), the mixture was stirred for 1 h, and the aq. phase was separated and extracted with $Et_2O$ (3 × 40 ml). The combined org. solns. were dried and concentrated to give a residue, which was purified by chromatography (elution with 8% AcOEt in petroleum): 231 mg (99%) of **16a**. White solid. M.p. 110–113°. $[\alpha]_D^{25} = +106$ ($c = 0.72$, $CHCl_3$). IR ($CHCl_3$): 3700–3100, 1658. $^1$H-NMR ($CDCl_3$): 5.64 (*dd*, $J = 8.2, 8.8$, 1 H); 3.90 (*m*, 1 H); 2.82 (*d*, $J = 12.6$, 1 H); 2.66 (*m*, 1 H); 2.42–2.25 (*m*, 2 H); 2.17–2.00 (*m*, 1 H); 2.00–1.63 (series of *m*, 10 H); 1.58 (*s*, 3 H); 1.56–1.28 (*m*, 2 H); 1.23 (*s*, 3 H); 1.09 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 218.5; 147.1; 121.2; 71.6; 53.0; 51.4; 48.1; 44.8; 41.1; 34.6; 33.8; 26.0; 25.5; 24.4; 21.9; 21.3; 20.6; 16.2. MS: $M^+$ calc.: 276.2089; observed: 276.2114. Anal. calc. for $C_{18}H_{28}O_2$: C 78.21, H 10.21; found: C 78.28, H 10.23.

*(1R,7aR,7R,10E,12aS)-1-[(tert-Butyl)dimethylsilyloxy]-2,3,4,4a,6,7,8,9,12,12a-decahydro-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5(1H)-one* (**16b**). A cold (0°), magnetically stirred soln. of **16a** (760 mg, 2.75 mmol) in $CH_2Cl_2$ (30 ml) containing $Et_3N$ (0.76 ml, 5.5 mmol) was treated with (*tert*-butyl)dimethylsilyl triflate (0.95 ml, 4.13 mmol), stirred for 3 h, and poured into brine (50 ml). The aq. phase was extracted with $Et_2O$ (3 × 50 ml), and the combined org. solns. were dried and concentrated. The residue was chromatographed (elution with 3% AcOEt in petroleum ether): 1.03 g (96%) of **16b** as a clear, colorless oil that solidified on standing. M.p. 67–68°. $[\alpha]_D^{22} = +29.3$ ($c = 0.7$, $CHCl_3$). IR ($CHCl_3$): 1667. $^1$H-NMR ($CDCl_3$): 5.58 (*t*, $J = 9.1$, 1 H); 3.83 (*m*, 1 H); 2.81 (*d*, $J = 12.5$, 1 H); 2.58 (*m*, 1 H); 2.41–2.33 (*m*, 1 H); 2.27–2.10 (*m*, 1 H); 2.10–1.99 (*m*, 1 H); 1.98–1.56 (series of *m*, 7 H); 1.56 (*s*, 3 H); 1.55–1.28 (series of *m*, 4 H); 1.24 (*s*, 3 H); 1.08 (*s*, 3 H); 0.93 (*s*, 9 H); 0.05 (*s*, 6 H). $^{13}$C-NMR ($CDCl_3$): 218.8; 146.7; 121.4; 72.4; 53.2; 51.4; 48.9; 44.7; 41.3; 34.6; 33.9; 26.2; 25.9; 25.6; 24.4; 21.9; 21.3; 20.8; 18.1; 16.5; –4.2; –5.2. MS: $M^+$ calc.: 390.2954; observed: 390.2934. Anal. calc. for $C_{24}H_{42}O_2Si$: C 73.79, H 10.83; found: C 73.65, H 10.82.

*(1R,4aR,5S,7R,10E,12aS)-1-[(tert-Butyl)dimethylsilyloxy]-1,2,3,4,4a,5,6,7,8,9,12,12a-dodecahydro-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5-ol* (**17a**). A soln. of **16b** (100 mg, 0.277 mmol) in benzene (25 ml) was treated with 0.27 ml of 1.0M DIBAH in hexane (0.27 mmol), stirred at r.t. for 30 min, and quenched with sat. $NH_4Cl$ soln. (20 ml). The separated aq. phase was extracted with $Et_2O$ (3 × 30 ml) and the combined org. layers were dried and concentrated. Chromatography of the residue (elution with 8% AcOEt in petroleum ether) gave **17a** (60 mg, 60%). White solid. M.p. 136–139°. $[\alpha]_D^{21} = -165$ ($c = 0.64$, $CHCl_3$). IR ($CHCl_3$): 3600. $^1$H-NMR ($CDCl_3$): 5.38 (*t*, $J = 7.8$, 1 H); 4.58 (*d*, $J = 10.2$, 1 H); 3.96 (*d*, $J = 2.7$, 1 H); 2.40–2.20 (*m*, 3 H); 2.17–2.03 (*m*, 3 H); 1.91–1.70 (*m*, 2 H); 1.70–1.50 (*m*, 6 H); 1.40–1.25 (*m*, 4 H); 1.34 (*s*, 3 H); 1.23 (*s*, 3 H); 1.18–1.07 (*m*, 2 H); 0.91 (*s*, 9 H); 0.05 (*s*, 3 H); 0.04 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 148.2; 119.5; 76.6; 74.0; 46.8; 46.2; 45.4; 41.7; 41.4; 35.3; 30.5; 29.8; 28.8; 26.4; 25.8; 24.3; 20.6; 19.7; 19.0; 16.2; –4.5; –5.0. MS: $[M - H_2O]^+$ calc.: 374.3005; observed: 374.3044. Anal. calc. for $C_{24}H_{44}O_2Si$: C 73.46, H 11.30; found: C 73.50, H 11.28.

*(1R,4aR,5S,10E,12aS)-1-[(tert-Butyl)dimethylsilyloxy]-1,2,3,4,4a,5,6,7,8,9,12,12a-dodecahydro-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5-yl Acetate* (**17b**). A soln. of **17a** (170 mg, 0.434 mmol) in pyridine (10 ml) was treated with $Ac_2O$ (5.0 ml) and 4-(dimethylamino)pyridine (20 mg), stirred overnight at r.t., diluted with AcOEt (50 ml), and washed with $H_2O$ (25 ml), 0.1N HCl (3 × 20 ml), and sat. $NaHCO_3$ soln. (20 ml). The org. layer was dried and concentrated, and the residue was chromatographed (elution with 3% AcOEt in petroleum ether): 157 mg (84%) of **17b**. White solid. M.p. 117–119°. $[\alpha]_D^{22} = -126$ ($c = 0.97$, $CHCl_3$). IR ($CHCl_3$): 1718. $^1$H-NMR ($CDCl_3$): 5.83 (*dd*, $J = 2.9, 10.4$, 1 H); 5.57 (*t*, $J = 7.6$, 1 H); 3.97 (*m*, 1 H); 2.35–2.29 (*m*, 2 H); 2.29–1.98 (*m*, 3 H); 1.96 (*m*, 3 H); 1.86–1.76 (*m*, 1 H); 1.76–1.52 (*m*, 6 H); 1.46 (*s*, 3 H); 1.46–1.31 (*m*, 4 H); 1.07 (*s*, 3 H); 1.06 (*s*, 3 H); 0.89 (*s*, 9 H); 0.04 (*s*, 3 H); 0.03 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 170.0; 148.8; 119.3; 80.4; 74.0; 46.7 (2 C); 45.0; 41.4; 38.5; 35.3; 31.5; 30.3; 28.2; 26.3; 25.8; 24.3; 21.1; 19.9; 19.6; 18.0; 16.2; –4.5; –5.0. MS: $M^+$ calc.: 434.3216; observed: 434.3255. Anal. calc. for $C_{26}H_{46}O_3Si$: C 71.83, H 10.66; found: C 72.01, H 10.76.

*(1R,4aR,5S,7R,10S,11S,12aS)-1-[(tert-Butyl)dimethylsilyloxy]perhydro-10,11-dihydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5-yl Acetate* (**18**). A soln. of **17b** (87.5 mg, 0.202 mmol) in pyridine (3 ml) was treated with 0.5 ml of an $OsO_4$ soln. (0.25 g in 2.5 ml of pyridine, 0.202 mmol), stirred overnight, and treated with sat. $NaHSO_3$ soln. (4 ml). After 4 h of stirring, the mixture was filtered and extracted with AcOEt (3 × 30 ml). The combined org. phases were washed with sat. $CuSO_4$ soln. (3 × 20 ml) and brine (30 ml), dried, and concentrated to give **18** (77.6 mg, 82%). White foam. M.p. 82–84°. $[\alpha]_D^{22} = -5.7$ ($c = 0.13$, $CHCl_3$). IR ($CHCl_3$): 3620–3240, 1720. $^1$H-NMR ($CDCl_3$): 5.32 (*dd*, $J = 4.4, 11.0$, 1 H); 4.20 (*d*, $J = 2.5$, 1 H); 3.98 (*t*, $J = 4.1$, 1 H); 2.48–2.34 (*m*, 4 H); 1.99 (*s*, 3 H); 1.95–1.85 (*m*, 2 H); 1.82–1.65 (*m*, 4 H); 1.65–1.42 (*m*, 8 H); 1.23 (*s*, 3 H); 1.07 (*s*, 3 H); 0.99 (*s*, 3 H); 0.98 (*s*, 9 H); 0.12 (*s*, 3 H); 0.05 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 170.7; 88.0; 80.3; 76.3; 71.6; 48.6; 47.6; 39.5; 37.0; 35.3; 34.3; 33.0; 32.3; 30.6; 29.8; 28.7; 25.8; 21.1; 18.5; 18.3; 18.0; 15.9; –4.5; –4.8. MS: $[M - OCOCH_3 - 2OH]^+$ calc.: 375.3015; observed: 375.3083. Anal. calc. for $C_{26}H_{48}O_5Si$: C 66.62, H 10.32; found: C 66.57, H 10.21.

*(1R,4aR,5S,7R,10R,11E,12aS)-1-[(tert-Butyl)dimethylsilyloxy]-1,2,3,4,4a,5,6,7,8,9,10,12a-dodecahydro-10-hydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5-yl 5-Acetate* (**19**). A soln. of **18** (22.9 mg, 0.05 mmol) in pyridine (1 ml) containing MsCl (20 µl, 0.26 mmol) was stirred overnight, diluted with $CH_2Cl_2$ (25 ml), washed with $H_2O$ (20 ml), 0.1N HCl (2 × 20 ml), and brine, then dried and concentrated. The residual oil was filtered through silica gel ($Et_2O$ elution) to give **19** (22 mg, 99%). White solid. M.p. 132–133.5°. The $^1$H-NMR of the unpurified reaction mixture indicated a 4:1 mixture of monomesylate and **19** to be present. Evidently, the former is transformed into **19** during the chromatography.

*Data of* **19**: $[\alpha]_D^{20} = -20.9$ ($c = 0.93$, $CHCl_3$). IR ($CHCl_3$): 3600, 1720. $^1$H-NMR ($CDCl_3$): 5.62 (*dd*, $J = 12.1$, 8.5, 1 H); 5.57 (*d*, $J = 12.1$, 1 H); 5.05 (*dd*, $J = 8.2$, 11.4, 1 H); 3.94 (*m*, 1 H); 2.44–2.31 (*m*, 3 H); 2.16–1.99 (*m*, 2 H); 1.97 (*s*, 3 H); 1.84–1.57 (*m*, 5 H); 1.52–1.25 (*m*, 5 H); 1.17 (*s*, 3 H); 1.12 (*s*, 3 H); 1.05 (*s*, 3 H); 0.90 (*s*, 9 H); 0.02 (*s*, 6 H). $^{13}$C-NMR ($CDCl_3$): 170.2; 139.1; 128.5; 84.7; 81.4; 70.9; 50.8; 48.0; 41.2; 39.8; 38.6; 35.4; 34.4; 30.6; 29.7; 29.0; 25.8; 21.1; 19.25; 19.18; 18.0; 16.3; –4.7; –5.0. MS: $[M - CH_3]^+$ calc.: 435.2930; observed: 435.2963.

*(1R,4aR,5S,7R,10S,11S,12aS)-1-[(tert-Butyl)dimethylsilyloxy]perhydro-4a,13,13-trimethyl-7,10-methanobenzocyclodecene-5,10,11-triol* (**20**) *and Its (5R)-Isomer* **21**. A soln. of **16b** (301 mg, 0.772 mmol) in pyridine (8 ml) was treated with $OsO_4$ (250 mg, 0.98 mmol), stirred for 2 d, and concentrated *in vacuo*. After addition of THF (20 ml), $LiAlH_4$ (204 mg, 7.72 mmol) was introduced and the mixture was stirred for 2 d, diluted with AcOEt (20 ml), and poured into sat. $NH_4Cl$ soln. (100 ml). More AcOEt (100 ml) was added, the mixture was filtered, and the separated aq. layer was extracted with AcOEt (3 × 50 ml). The combined org. solns. were dried and concentrated to leave a residue, chromatography of which (elution with 40% AcOEt in petroleum ether) gave a 1:1 mixture **20**/**21** (285 mg, 87%). These epimers were separated by flash chromatography on TLC-grade silica gel, **20** being less polar.

*Data of* **20**: white solid. M.p. 162–163°. $[\alpha]_D^{21} = +1.5$ ($c = 0.16$, $CHCl_3$). IR ($CHCl_3$): 3620. $^1$H-NMR ($CDCl_3$): 4.20 (*d*, $J = 2.5$, 1 H); 3.99 (*dd*, $J = 3.7$, 11.5, 1 H); 3.91 (*t*, $J = 4.0$, 1 H); 2.50–2.34 (*m*, 3 H); 2.05–1.86 (*m*, 1 H); 1.86–1.65 (*m*, 5 H); 1.65–1.45 (*m*, 4 H); 1.45–1.32 (*m*, 2 H); 1.32–1.15 (*m*, 4 H); 1.15 (*s*, 3 H); 1.13 (*s*, 3 H); 1.08 (*s*, 3 H); 0.92 (*s*, 9 H); 0.12 (*s*, 3 H); 0.06 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 88.3; 78.0; 76.9; 71.7; 49.0; 47.7; 39.9; 39.4; 37.7; 34.3; 33.2; 32.3; 29.3; 29.1; 28.7; 25.9; 18.9; 18.5; 18.1; 16.1; –4.5; –4.8. MS: $[M - 2\,H_2O - CH_3]^+$ calc.: 375.2719; observed: 375.2682. Anal. calc. for $C_{24}H_{46}O_4Si$: C 67.55, H 10.86; found: C 67.31, H 10.84.

*Data of* **21**: white solid. M.p. 205–206°. $[\alpha]_D^{21} = -0.50$ ($c = 0.11$, $CHCl_3$). IR ($CHCl_3$): 3618, 3565. $^1$H-NMR ($CDCl_3$): 4.08 (*d*, $J = 2.6$, 1 H); 3.71 (*d*, $J = 6.6$, 1 H); 3.40 (*d*, $J = 7.4$, 1 H); 2.51–2.40 (*m*, 1 H); 2.40–2.15 (*m*, 2 H); 2.15–2.06 (*m*, 2 H); 1.90–1.60 (series of *m*, 5 H); 1.60–1.41 (*m*, 5 H); 1.40–1.25 (*m*, 3 H); 1.15–1.05 (*m*, 1 H); 1.10 (*s*, 3 H); 1.03 (*s*, 3 H); 0.97 (*s*, 3 H); 0.92 (*s*, 9 H); 0.10 (*s*, 3 H); 0.05 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 87.5; 79.5; 75.5; 72.7; 47.8; 45.2; 40.3; 39.6; 38.5; 34.1; 33.1; 32.3; 30.7; 26.8; 25.9; 22.6; 18.1; 17.6; 16.1; 12.7; –4.4; –4.9. MS: $[M - H_2O - CH_3]^+$ calc.: 393.2825; observed: 393.2846. Anal. calc. for $C_{24}H_{46}O_4Si$: C 67.55, H 10.86; found: C 67.33, H 10.84.

*(1R,4aR,5R,7R,10S,11S,12aS)-1-[(tert-Butyl)dimethylsilyloxy]perhydro-10-hydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecene-5,11-diyl Diacetate* (**22a**). A soln. of **21** (398 mg, 0.93 mmol) in pyridine (10 ml) containing 4-(dimethylamino)pyridine (10 mg) was treated with $Ac_2O$ (5 ml, 53 mmol), stirred at r.t. overnight, diluted with AcOEt (50 ml), and washed with $H_2O$ (50 ml), 0.1N HCl (2 × 25 ml), sat. $NaHCO_3$ soln. (2 × 20 ml), and brine (30 ml). After drying and concentration, the residue was chromatographed (elution with 10% AcOEt in petroleum ether): 381 mg (80%) of **22a**. White foam. M.p. 78–80°. $[\alpha]_D^{21} = +8.8$ ($c = 0.73$, $CHCl_3$). IR ($CHCl_3$): 3562, 1718. $^1$H-NMR ($CDCl_3$): 5.05 (*d*, $J = 6.7$, 1 H); 4.72 (*d*, $J = 7.6$, 1 H); 3.74 (*s*, 1 H); 2.47–2.04 (series of *m*, 7 H); 2.03 (*s*, 3 H); 1.96 (*s*, 3 H); 1.81–1.57 (*m*, 5 H); 1.47–1.19 (*m*, 5 H); 1.07 (*s*, 3 H); 1.06 (*s*, 3 H); 1.01 (*s*, 3 H); 0.86 (*s*, 9 H); –0.01 (*s*, 3 H); –0.04 (*s*, 3 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 171.0; 170.3; 86.3; 81.6; 77.9; 72.7; 48.7; 45.9; 39.8; 39.0; 38.3; 33.9; 33.8; 31.3; 30.4; 25.9; 25.8; 22.4; 21.3; 21.2; 18.0; 17.9; 15.7; 13.6; –4.4; –5.3. MS: $[M - H_2O]^+$ calc.: 492.3271; observed: 492.3281. Anal. calc. for $C_{28}H_{50}O_6Si$: C 65.85, H 9.87; found: C 65.77, H 9.86.

*(1R,4aR,5R,7R,10S,11S,12aS)-1-[(tert-Butyl)dimethylsilyloxy]perhydro-10,11-dihydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5-yl Acetate* (**22b**). A soln. of **22a** (74 mg, 0.145 mmol) in MeOH/$H_2O$ (5 ml of 1:1) was treated with $K_2CO_3$ (40 mg, 0.289 mmol), stirred overnight at r.t., and evaporated *in vacuo*. The residue was filtered through silica gel (elution with 30% AcOEt in petroleum ether) to provide 39 mg (57%) of **22b** as a white solid. M.p. 65–66°. $[\alpha]_D^{23} = +6.7$ ($c = 0.52$, $CHCl_3$). IR ($CHCl_3$): 3610, 3565, 1718. $^1$H-NMR ($CDCl_3$): 4.73 (*d*, $J = 8.1$, 1 H); 4.08 (*d*, $J = 2.4$, 2 H); 3.71 (*d*, $J = 6.7$, 1 H); 2.57–2.45 (*m*, 1 H); 2.35–2.20 (*m*, 3 H); 2.2–2.0 (*m*, 3 H); 1.99 (*s*, 3 H); 1.95–1.75 (*m*, 1 H); 1.70–1.40 (*m*, 6 H); 1.40–1.10 (*m*, 4 H); 1.09 (*s*, 3 H); 1.05 (*s*, 3 H); 1.02 (*s*, 3 H); 0.92 (*s*, 9 H); 0.10 (*s*, 3 H); 0.04 (*s*, 3 H). $^{13}$C-NMR (62.5 MHz, $CDCl_3$): 170.5; 87.6; 82.0; 75.3; 72.4; 47.9; 45.5; 39.6; 38.8; 38.1; 33.9; 33.1; 30.7; 30.4; 26.4; 25.9; 22.1; 21.3; 18.0; 17.6; 15.8; 13.7; –4.4; –4.9. MS: [*M* – (*t*-

Bu) – $H_2O$]$^+$ calc.: 393.2461; observed: 393.2587. Anal. calc. for $C_{26}H_{48}O_5Si$: C 66.62, H 10.32; found: C 66.30, H 10.20.

*(1*R*,4a*R*,5*R*,7*R*,10*S*,11*S*,12a*S*)-1-[(*tert*-Butyl)dimethylsilyloxy]perhydro-10-hydroxy-11-(methanesulfonyloxy)-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5-yl Acetate* (**22c**). To a soln. of **22b** (20.1 mg, 0.043 mmol) in pyridine (1 ml) was added MsCl (20 µl, 0.26 mmol), and the mixture was stirred overnight at r.t., diluted with $CH_2Cl_2$ (25 ml), and washed sequentially with $H_2O$ (20 ml), 0.1N HCl (2 × 20 ml); and brine (20 ml). After drying and concentration, the residue was filtered through silica gel to give **22c** (24 mg, 100%). White solid. M.p. 125–129° (dec.). $[\alpha]_D^{21} = +4.5$ ($c = 0.60$, $CHCl_3$). IR ($CHCl_3$): 3590–3460, 1720, 1348, 1174. $^1$H-NMR ($CDCl_3$): 4.78 (*d*, *J* = 7.5, 1 H); 4.67 (*d*, *J* = 6.7, 1 H); 4.04 (*m*, 1 H); 3.11 (*s*, 3 H); 2.60–2.42 (*m*, 2 H); 2.42–2.02 (series of *m*, 6 H); 2.00 (*s*, 3 H); 1.88–1.56 (*m*, 5 H); 1.56–1.17 (*m*, 4 H); 1.11 (*s*, 3 H); 1.08 (*s*, 3 H); 1.06 (*s*, 3 H); 0.91 (*s*, 9 H); 0.13 (*s*, 3 H); 0.07 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 170.3; 88.9; 86.4; 81.4; 72.8; 48.9; 46.3; 40.0; 39.4; 38.7; 37.6; 34.8; 33.8; 31.3; 30.4; 28.0; 26.0; 23.0; 21.3; 18.0; 15.9; 13.6; 1.0; –4.6; –5.0. MS: [*M* – (*t*-Bu) – $CH_3SO_3H$]$^+$ calc.: 393.2429; observed: 393.2393. Anal. calc. for $C_{27}H_{50}O_7SSi$: C 59.30, H 9.22; found: C 59.11, H 9.23.

*(4*R*,4a*S*,6*S*,10*R*,12*R*,12a*R*)-4-[(*tert*-Butyl)dimethylsilyloxy]perhydro-12a,13,13-trimethyl-7-oxo-6,10-methano-1*H*-benzocyclodecen-12-yl Acetate* (**23**) *and (1*R*,4a*R*,5*R*,7*R*,10*R*,11*E*,12a*S*)-1-[(*tert*-Butyl)dimethylsilyloxy]-1,2,3,4,4a,5,6,7,8,9,10,12a-dodecahydro-10-hydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5-yl Acetate* (**24**). A soln. of unpurified **22c** (58 mg, 0.106 mmol) in cold (–78°) $CH_2Cl_2$ (5 ml) was treated with $Et_2AlCl$ (0.53 ml of 1.0M in hexane, 0.53 mmol) and stirred for 4 h. MeOH (2 ml) was introduced, the mixture was poured into $H_2O$ (50 ml), and the aq. phase was extracted with $Et_2O$ (3 × 20 ml). The combined org. layers were washed with brine, dried, and evaporated. The residue (42.5 mg, 88%) was a 1:1 mixture **23**/**24**. The first product could be obtained pure by chromatography (elution with 10% AcOEt in petroleum ether).

*Data of* **23**: colorless oil. $^1$H-NMR ($CDCl_3$): 4.75 (*d*, *J* = 9.6, 1 H); 3.60 (*m*, 1 H); 2.60–2.10 (series of *m*, 6 H); 2.01 (*s*, 3 H); 1.80–1.14 (series of *m*, 10 H); 1.15 (*s*, 3 H); 1.08 (*s*, 3 H); 1.00–0.80 (*m*, 1 H); 0.89 (*s*, 3 H); 0.88 (*s*, 9 H); 0.02 (*s*, 3 H); 0.01 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 216.3; 170.3; 81.0; 76.9; 56.6; 44.0; 40.2; 38.2; 37.6; 37.4; 36.9; 34.2; 32.4; 32.1; 28.5; 26.1; 25.8; 21.7; 21.4; 18.1; 16.1; 14.2; –4.3; –5.1. MS: [*M* – $C_4H_8$]$^+$ calc.: 394.2539; observed: 394.2489.

Since **24** could not be obtained free of **23**, the 1:1 mixture of acetates was dissolved in MeOH/THF 4:1 (2 ml), treated with LiOH (0.1 ml of 2.5M in $H_2O$, 0.25 mmol), and allowed to stir at r.t. for 72 h. The mixture was diluted with AcOEt (20 ml) and poured into $H_2O$ (20 ml). The aq. phase was extracted with AcOEt (3 × 20 ml) and the combined org. layers were washed with brine, dried, and concentrated. The residue was chromatographed (elution with 20% AcOEt in petroleum ether) to afford pure diol corresponding to **24** (9.0 mg, 56%) as a white solid. M.p. 171–173°. $^1$H-NMR ($CDCl_3$): 5.72 (*dd*, *J* = 12.9, 13.0, 1 H); 5.47 (*d*, *J* = 13.4, 1 H); 3.78 (*m*, 1 H); 3.59 (*d*, *J* = 7.6, 1 H); 2.60 (*dt*, *J* = 15.7, 7.4, 1 H); 2.28 (*dd*, *J* = 2.5, 11.5, 1 H); 2.17–1.69 (series of *m*, 6 H); 1.55–1.40 (*m*, 2 H); 1.40–1.08 (series of *m*, 6 H); 1.04 (*s*, 3 H); 1.01 (*s*, 3 H); 0.96 (*s*, 3 H); 0.92 (*s*, 9 H); 0.03 (*s*, 6 H). $^{13}$C-NMR ($CDCl_3$): 135.3; 131.2; 83.1; 79.5; 72.0; 47.4; 42.8; 41.4; 40.7; 40.0; 34.9; 34.4; 31.1; 29.7; 25.9; 25.6; 23.0; 17.8 15.8; 13.3; –4.6; –4.9.

*(2*S*,3a*S*,5*S*,6a*S*,7*R*,10a*S*,10b*R*)-7-[(*tert*-Butyl)dimethylsilyloxy]perhydro-10a,11,11-trimethyl-2,5-methanobenz[e]azulen-4(1*H*)-one* (**26**). Compound **22c** (30 mg, 0.055 mmol) was added to a soln. of *t*-BuOK in *t*-BuOH (1 ml of 2.5M, 0.25 mmol), heated at reflux for 30 min, cooled, and poured into AcOH/$H_2O$ 1:1 (20 ml). The product was extracted into $Et_2O$ (3 × 20 ml) and the combined org. phases were washed with $H_2O$ (2 × 20 ml), sat. $NaHCO_3$ soln. (20 ml), and brine (20 ml) prior to drying and evaporation. The residue was chromatographed (elution with 5% AcOEt in petroleum ether): 10.7 mg (50%) of **26**. Clear, colorless oil. IR ($CHCl_3$): 1692. $^1$H-NMR ($CDCl_3$): 4.05 (*m*, 1 H); 2.80–2.55 (*m*, 1 H); 2.40–2.20 (*m*, 1 H); 2.10–2.00 (*m*, 4 H); 1.96–1.89 (*m*, 1 H); 1.70–1.65 (*m*, 5 H); 1.50–1.20 (*m*, 5 H); 1.07 (*s*, 3 H); 1.02 (*s*, 3 H); 0.89 (*s*, 9 H); 0.85 (*s*, 3 H); 0.01 (*s*, 3 H); 0.01 (*s*, 3 H). $^{13}$C-NMR (50 MHz, $CDCl_3$): 213.7; 69.8; 69.3; 62.5; 55.0; 49.0; 43.5; 41.1; 41.0; 33.9; 30.9; 29.7; 26.6; 26.3; 25.8; 22.9; 22.2; 18.1; 16.4; –4.8; –5.1. MS: $M^+$ calc.: 390.2954; observed: 390.3013.

*(4*R*,4a*S*,7*S*,10*R*,12*S*,12a*R*)-4-[(*tert*-Butyl)dimethylsilyloxy]perhydro-7-hydroxy-12a,13,13-trimethyl-6-oxo-7,10-methano-2*H*-benzocyclodecen-12-yl Acetate* (**27**). A soln. of DMSO (27 µl, 0.384 mmol) in $CH_2Cl_2$ (3 ml) was cooled to –78° and treated dropwise during 5 min with oxalyl chloride (17 µl, 0.192 mmol) dissolved in $CH_2Cl_2$ (3 ml). A soln. of **18** (45 mg, $9.61 \times 10^{-5}$ mol) in $CH_2Cl_2$ (5 ml) was next introduced during 10 min. The cloudy mixture was stirred at –78° for 15 min, before $Et_3N$ (80 µl, 0.576 mmol) was added, allowed to warm to r.t., and stirred for 2 h. After dilution with $H_2O$, the layers were separated, and the org. phase was washed with $H_2O$ and brine prior to drying and evaporation. Chromatography of the residue on silica gel (elution with 20% AcOEt in petroleum ether) furnished **27** as a white solid (34 mg, 76%). M.p. 196–198°. $[\alpha]_D^{20} = -20.2$ ($c = 1.1$, $CHCl_3$). IR ($CHCl_3$): 3520, 1720, 1675, 1250. $^1$H-NMR ($CDCl_3$): 4.72 (*d*, *J* = 10.9, 1 H); 3.99 (*d*, *J* = 2.6, 1 H); 2.99 (*s*, 1 H); 2.87 (*dd*, *J* = 15.7, 12.1, 1 H); 2.49–2.43 (*m*, 2 H); 2.26–2.18 (*m*, 3 H); 2.17–1.66 (series of *m*, 3 H); 1.96 (*s*, 3 H);

1.63–1.55 (*m*, 3 H); 1.50–1.38 (*m*, 2 H); 1.29–1.23 (*m*, 2 H); 1.13 (*s*, 3 H); 1.09 (*s*, 3 H); 1.08 (*s*, 3 H); 0.88 (*s*, 9 H); 0.05 (*s*, 3 H); 0.04 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 217.3; 169.4; 87.4; 78.9; 73.2; 49.0; 46.8; 46.1; 39.5; 38.0; 35.1 (2 C); 31.7; 31.0; 29.3 (2 C); 25.8; 20.9; 19.3; 19.0; 18.0; 15.7; –4.4, –5.0. FAB-MS: $[M - 1]^+$ calc.: 467.33; observed: 467.32. Anal. calc. for $C_{26}H_{46}O_5Si$: C 66.91, H 9.93; found: C 66.70, H 9.98.

*Equilibration Studies Involving* **27**. a) *Short Reaction Time*. A soln. of **27** (18.8 mg, 40.3 μmol) and (i-PrO)$_3$Al (25 mg, 12.1 mmol) in dry benzene (5 ml) was blanketed with $N_2$ and heated at 50° while magnetically stirred. After 60 min, the mixture was diluted with $H_2O$ and AcOEt, and the separated org. phase was washed with 1M HCl, water, and brine. After drying and solvent evaporation, the residue was chromatographed on silica gel (elution with 12% AcOEt in petroleum ether) to give in order of elution 7.8 mg (42%) of **28**, 3.2 mg (17%) of **27**, and 7.1 mg (38%) of **29**.

b) *Intermediate Reaction Time*. A soln. of **27** (9.2 mg, 19.7 μmol) and (i-PrO)$_3$Al (12.1 mg, 59.2 mmol) in dry benzene (3 ml) was refluxed under $N_2$ for 3 h. The usual workup and chromatography afforded 1.1 mg (12%) of **28** followed by 7.6 mg (83%) of **29**.

c) *Prolonged Heating*. A soln. of **27** (18.3 mg, $3.92 \times 10^{-5}$ mol) and ($t$-BuO)$_3$Al (29 mg, $1.18 \times 10^{-4}$ mol) in dry benzene (4 ml) was heated at reflux under $N_2$ for 12 h. These conditions provided for the isolation of **29** (17.0 mg, 93%) as the only eluant.

*Data of (4*R*,4a*S*,6*R*,10*R*,12*S*,12a*R*)-4-[(*tert*-Butyl)dimethylsilyloxy]perhydro-6-hydroxy-12a,13,13-trimethyl-7-oxo-6,10-methano-1*H*-benzocyclodecen-12-yl Acetate* (**28**): colorless solid. M.p. 148.5–150°. $[\alpha]_D^{21} = +25.1$ ($c = 2.7$, $CHCl_3$). IR ($CHCl_3$): 3503, 1725, 1697, 1220. $^1$H-NMR ($C_6D_5Br$, 420 K): 5.16 (*d*, $J = 9.3$, 1 H); 3.52 (*m*, 1 H); 3.39 (br. *s*, 1 H); 2.42 (*dd*, $J = 2.9$, 8.4, 1 H); 2.48–2.33 (*m*, 1 H); 2.23 (*dd*, $J = 16.0$, 6.2, 1 H); 2.12 (*m*, 1 H); 1.98–1.87 (*m*, 2 H); 1.77 (*s*, 3 H); 1.80–1.50 (series of *m*, 4 H); 1.47 (*m*, 2 H); 1.45–1.26 (series of *m*, 4 H); 1.29 (*s*, 3 H); 1.03 (*s*, 3 H); 0.84 (*s*, 3 H); 0.79 (*s*, 9 H); –0.06 (*s*, 3 H); –0.10 (*s*, 3 H). $^{13}$C-NMR ($C_6D_5Br$, 360 K): 218.3; 172.3; 84.6; 82.7 (br.); 77.4 (br.); 45.8; 44.3 (br.); 43.5; 42.1; 39.7; 38.0; 35.0; 33.2; 33.0 (br.); 30.8 (br.); 29.1; 25.9; 25.5; 23.9; 22.6; 21.2; 19.3; –1.2; –1.8. FAB-MS: $[M + 1]^+$ calc.: 467.31; observed: 467.29.

*Data of (4*R*,4a*S*,6*R*,9*R*,11*S*,11a*R*)-4-[(*tert*-Butyl)dimethylsilyloxy]perhydro-6-hydroxy-8,8,11a-trimethyl-7-oxo-6,9-ethano-7*H*-benzocyclononen-12-yl Acetate* (**29**): colorless solid. M.p. 164–166°. $[\alpha]_D^{21} = -14.1$ ($c = 2.7$, $CHCl_3$). IR ($CHCl_3$): 3540, 1730, 1700, 1250. $^1$H-NMR ($C_6D_6$): 4.92 (*d*, $J = 9.6$, 1 H); 3.84 (*d*, $J = 2.8$, 1 H); 3.62 (*s*, 1 H); 2.38 (*dd*, $J = 15.4$, 7.1, 1 H); 2.16–1.67 (series of *m*, 10 H); 1.65 (*s*, 3 H); 1.53 (*m*, 2 H); 1.35 (*s*, 3 H); 1.36–0.93 (series of *m*, 3 H); 1.15 (*s*, 3 H); 1.06 (*s*, 3 H); 0.94 (*s*, 9 H); 0.08 (*s*, 3 H); 0.02 (*s*, 3 H). $^{13}$C-NMR ($C_6D_6$): 220.6; 168.6; 76.5; 76.2; 76.1; 46.8; 45.6; 40.7; 40.4; 39.9; 37.3; 35.2; 30.8; 30.0; 28.5; 26.7; 26.0; 22.5; 20.5; 19.7; 18.2; 16.1; –4.3; –4.9. FAB-MS: $[M + 1]^+$ calc.: 467.31; observed: 467.38.

*(1*R*,4a*R*,7*R*,10*S*,11*S*,12a*S*)-1-[(*tert*-Butyl)dimethylsilyloxy]perhydro-10,11-dihydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecen-5(1*H*)-one* (**30**). A soln. of **16b** (1.12 g, 2.87 mmol) in dry pyridine (30 ml) was treated under $N_2$ with 8.0 ml of 0.393M $OsO_4$ in pyridine *via* syringe. The resulting black mixture was stirred at r.t. for 13 h, treated with sat. $NaHSO_3$ soln. (50 ml), and stirred for an additional 90 min. After filtration through *Celite*, the residue was washed with copious amounts of $CH_2Cl_2$. The aq. layer was extracted with $CH_2Cl_2$ (3×) and the combined org. solns. were washed with brine, dried, and concentrated. The residual oil was purified by chromatography on silica gel (elution with AcOEt/petroleum ether 1:1): 1.13 g (93%) of **30**. Colorless solid. M.p. 160.5–161° (from AcOEt). $[\alpha]_D^{20} = +27.5$ ($c = 0.68$, $CHCl_3$). IR ($CHCl_3$): 3620, 3560, 1670, 1250. $^1$H-NMR ($CDCl_3$): 4.05 (*d*, $J = 2.5$, 1 H); 3.75 (*dd*, $J = 1.5$, 6.8, 1 H); 3.10 (*dd*, $J = 9.6$, 19.9, 1 H); 2.40–1.99 (*m*, 7 H); 1.99–1.27 (series of *m*, 10 H); 1.22 (*s*, 3 H); 1.10 (*s*, 3 H); 0.92 (*s*, 9 H); 0.90 (*s*, 3 H); 0.11 (*s*, 3 H); 0.06 (*s*, 3 H). $^{13}$C-NMR (62.5 MHz, $CDCl_3$): 217.0; 86.4; 73.6; 73.4; 51.5; 48.2; 45.6; 39.4; 36.9; 34.9; 33.9; 32.7; 29.9; 25.9; 24.2; 18.04; 18.02; 17.95; 15.9; –4.4; –5.0. MS: $M^+$ calc.: 424.3009; observed: 424.3011. Anal. calc. for $C_{24}H_{44}O_4Si$: C 67.87, H 11.17; found: C 68.13, H 10.47.

*(1*R*,4a*R*,7*R*,10*S*,12a*S*)-1-[(*tert*-Butyl)dimethylsilyloxy]perhydro-10-hydroxy-4a,13,13-trimethyl-7,10-methanobenzocyclodecene-5,11(1*H*,6*H*)-dione* (**31**). A soln. of DMSO (6.74 ml, 10.2 mmol) in $CH_2Cl_2$ (15 ml) was cooled to –78° and treated dropwise during 15 min with oxalyl chloride (0.45 ml, 5.20 mmol) dissolved in $CH_2Cl_2$ (10 ml). A soln. of **30** (1.10 g, 2.60 mmol) in $CH_2Cl_2$ (30 ml) was next introduced during 25 min. The cloudy mixture was stirred for 10 min at –78°, before $Et_3N$ (2.17 ml, 15.6 mmol) was added, allowed to warm to r.t., and stirred for 1 h. The customary workup gave a yellowish solid, recrystallization of which from hexane afforded **31** (975 mg, 89%). Colorless crystals. M.p. 194.5–196°. $[\alpha]_D^{21} = -32.1$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3560, 1690, 1260. $^1$H-NMR ($CDCl_3$): 4.00 (*d*, $J = 2.7$, 1 H); 3.23 (*s*, 1 H); 3.03 (*dd*, $J = 14.6$, 8.7, 1 H); 2.79 (*dd*, $J = 13.6$, 6.4, 1 H); 2.68 (*d*, $J = 4.3$, 1 H); 2.64 (*d*, $J = 3.9$, 1 H); 2.44 (*m*, 1 H); 2.33 (*ddd*, $J = 7.8$, 4.3, 4.3, 1 H); 2.19 (*m*, 1 H); 2.02 (*m*, 1 H); 1.81–1.64 (series of *m*, 5 H); 1.49 (*d*, $J = 1.5$, 1 H); 1.45 (br. *s*, 1 H); 1.27 (*m*, 1 H); 1.26 (*s*, 3 H); 1.12 (*s*, 3 H); 1.07 (*s*, 3 H); 0.91 (*s*, 9 H); 0.09 (*s*, 3 H); 0.07 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 216.1; 215.4; 87.9; 71.6; 52.0; 49.9; 46.7; 43.9;

41.9; 39.0; 36.0; 34.3; 33.7; 29.5; 27.6; 25.8; 19.2; 18.0; 17.2; 15.7; –4.4; –5.1. FAB-MS: $[M + 1]^+$ calc.: 423.29; observed: 423.44. Anal. calc. for $C_{24}H_{42}O_4Si$: C 68.20, H 10.02; found: C 68.02, H 9.96.

*Equilibration Studies Involving* **32**. a) *Benzene at r.t.* A soln. of **31** (17 mg, $4.02 \times 10^{-5}$ mol) and (*t*-BuO)$_3$Al (30 mg, 0.121 mmol) in dry benzene (5 ml) was stirred under $N_2$ at r.t. for 4 h and diluted with 1M HCl and AcOEt. The org. phase was washed with $H_2O$ and brine. The original aq. phase was extracted with AcOEt and the combined nonaqueous fractions were dried and evaporated to leave a solid. Chromatography of this material on silica gel (elution with 10% AcOEt in petroleum ether) furnished 9.2 mg (54%) of **32** and 5.9 mg (35%) of **33**.

b) *THF at r.t.* A soln. of **31** (5.4 mg, $1.28 \times 10^{-5}$ mol) and (*t*-BuO)$_3$Al (9.4 mg, $3.84 \times 10^{-5}$ mol) in dry THF (3 ml) was stirred at r.t. for 12 h and processed as described above. The distribution within the resulting three-component mixture was determined by 300-MHz $^1$H-NMR to be 17% of **31**, 47% of **32**, and 36% of **33**. The protons geminal to the TBSO substituent are sufficiently distinctive in the three isomers to permit ready integration.

c) *Benzene at the Reflux. Temp.* A soln. of **31** (920 mg, 2.18 mmol) and (*t*-BuO)$_3$Al (1.61 g, 6.53 mmol) in dry benzene (50 ml) was heated to reflux under $N_2$ for 4 h. The cooled mixture was processed as before to give 800 mg (87%) of **32** as the only isolated product.

*Data of (4*R*,4a*S*,6*R*,10*R*,12a*R*)-4-[(*tert*-Butyl)dimethylsilyloxy]perhydro-6-hydroxy-12a,13,13-trimethyl-6,10-methanobenzocyclodecene-7,12-dione* (**32**): colorless crystals. M.p. 151–153° (from AcOEt). $[\alpha]_D^{21} = -1.7$ ($c$ = $CHCl_3$). IR ($CHCl_3$): 3520, 1735, 1700, 1265. $^1$H-NMR ($CDCl_3$): 3.78 (*s*, 1 H); 3.67 (*d*, $J$ = 2.6, 1 H); 3.00 (*dd*, $J$ = 12.5, 6.1, 1 H); 2.59 (*m*, 3 H); 2.45–2.14 (series of *m*, 3 H); 1.97 (*m*, 1 H); 1.80–1.50 (series of *m*, 3 H); 1.45 (*s*, 3 H); 1.49–1.16 (series of *m*, 4 H); 1.14 (*s*, 3 H); 0.95 (*s*, 3 H); 0.94–0.81 (*m*, 1 H); 0.90 (*s*, 9 H); 0.58 (*s*, 3 H); 0.03 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 217.8; 215.9; 83.0; 75.8; 52.1; 43.7; 43.0; 42.1; 41.9; 38.0; 36.8; 35.7; 34.4; 29.0; 25.8; 24.9; 22.9; 18.0; 17.7; 15.7; –4.4; –5.0. FAB-MS: $[M + 1]^+$ calc.: 423.29; observed: 423.31. Anal. calc. for $C_{24}H_{42}O_4Si \cdot 0.5\ C_4H_8O_2$ (AcOEt of solvation): C 66.91, H 9.93; found: C 66.96, H 9.91.

*Data of (4*R*,4a*S*,6*R*,9*R*,11a*R*)-4-[(*tert*-Butyl)dimethylsilyloxy]perhydro-6-hydroxy-8,8,11a-trimethyl-6,9-ethano-1*H*-benzocyclononene-7,11(2*H*,8*H*)-dione* (**33**): colorless crystals. M.p. 185–188° (from AcOEt). $[\alpha]_D^{21} = -18.2$ ($c$ = 1.8, $CHCl_3$). IR ($CHCl_3$): 3520, 1740, 1700, 1270. $^1$H-NMR ($CDCl_3$): 3.97 (*d*, $J$ = 2.7, 1 H); 3.16 (*s*, 1 H); 2.83 (*dd*, $J$ = 12.8, 3.3, 1 H); 2.65 (*m*, 1 H); 2.50 (*m*, 1 H); 2.40 (*dd*, $J$ = 8.8, 3.3, 1 H); 2.25–2.00 (series of *m*, 4 H); 1.90–1.62 (series of *m*, 2 H); 1.60–1.03 (series of *m*, 4 H); 1.41 (*s*, 3 H); 1.32 (*s*, 3 H); 1.18 (*s*, 3 H); 0.93–0.78 (*m*, 2 H); 0.90 (*s*, 9 H); 0.08 (*s*, 3 H); 0.06 (*s*, 3 H). $^{13}$C-NMR ($CDCl_3$): 218.7; 215.7; 75.3; 74.6; 52.0; 48.1; 45.5; 42.8; 40.1; 38.5; 36.2; 34.4; 29.6; 28.0; 25.8; 22.8; 18.0; 16.8; 15.6 (2 C); –4.4; –5.0. FAB-MS: $[M + 1]^+$ calc.: 423.29; observed: 423.31. Anal. calc. for $C_{24}H_{42}O_4Si \cdot 0.5\ C_4H_8O_2$ (AcOEt of solvation): C 66.91, H 9.93; found: C 66.89, H 9.86.

*Supplementary Material.* Final atomic coordinates for the compounds displayed in *Figs. 1–3*.

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