tane-ether, 95:9). ^{1}H NMR: δ 2.37 (s, 3 H), 2.65-3.4 (m, 2 H), 3.95 (ddd, J = 11.2, 9.0, and 4.0 Hz, 1 H), 4.24 (ddd, J = 11.2, 6.0, and 4.0 Hz, 1 H), 5.95 (br s, 1 H), 6.65-7.35 (m, 8 H). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.61; H, 7.22. This compound should be formed by Sommelet rearrangement of the ylide **61b** but was not detected among the reaction products of **55b**.

2-(1,3-Dioxolan-2-yl)benzaldehyde Tosylhydrazone (69). The tosylhydrazone **69** was obtained from the analogous aldehyde **68**[35] in 94% yield as described previously in the preparation of **14**; mp 129-131 °C. ^{1}H NMR: δ 2.37 (s, 3 H), 3.8-4.2 (m, 4 H), 5.83 (s, 1 H), 7.3-7.85 (m, 8 H), 8.31 (s, 1 H), 11.45 (br s, 1 H). Anal. Calcd for $C_{17}H_{18}N_2O_4S$: C 58.94; H, 5.24; N, 8.09. Found: C, 58.88; H, 5.32; N, 8.17.

The sodium salt of **69** was prepared and flash-pyrolyzed as described previously for **15**. Pyrolysis of 1.2 g (3.25 mmol) of the sodium salt afforded 0.35 g (66%) of volatile products. Spiro[bicyclo[4.2.0]octa-1,3,5-triene-7,2'-[1,3]dioxolane] (**70**)[20] and phthalaldehyde were identified by comparison (GC) with authentic samples. Separation by HPLC (silica gel, *n*-hexane-ether, 8:2) yielded 1,4-epoxy-1,3,4,5-tetrahydro-2-benzoxepin (**72**) [^{1}H NMR: δ 2.58 (br d, J = 17.0 Hz, 1 H), 3.37 (br dd, J = 17.0 and 4.6 Hz, 1 H), 3.66 (dd, J = 7.3 and 4.6 Hz, 1 H), 3.96 (dd, J = 7.3 and 6.1 Hz, 1 H), 4.83 (dddd, J = 6.1, 4.6, 1.9, and 0.8 Hz, 1 H), 5.97 (s, 1 H), 7.05-7.25 (m, 4 H)], 2,3,4a,8b-tetrahydrobenzo-[3,4]cyclobuta[1,2-*b*]dioxin (**75**) [^{1}H NMR: δ 3.74 (s, 4 H), 5.34 (s, 2 H), 7.35 (br s, 4 H). ^{13}C NMR: δ 61.7, 73.8, 123.7, 129.9, 145.8. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.97; H, 6.26.], and 2-(1,3-dioxolan-2-yl)benzonitrile[52] (9-10%).

Photolyses of **69** in NaOMe-MeOH were carried out as described for **14**. The major products were isolated by HPLC (silica gel, *n*-pentane-ether, 9:1). 2-[2-(Methoxymethyl)phenyl]-1,3-dioxolane (**73**, R = CH_3): ^{1}H NMR δ 3.37 (s, 3 H), 3.95-4.15 (m, 4 H), 4.60 (s, 2 H), 6.05 (s, 1 H), 7.25-7.65 (m, 4 H). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.04; H, 7.10. 1-Methoxy-1,3,4,6-tetrahydro-2,5-benzodioxocin (**76**, R = CH_3): ^{1}H NMR δ 3.32 (s, 3 H), 3.3-3.8 (m, 4 H), 4.58 (d, J = 12.4 Hz, 1 H), 5.04 (d, J = 12.4 Hz, 1 H), 5.58 (s, 1 H), 7.0-7.25 (m, 3 H), 7.7-7.85 (m, 1 H). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.16; H, 7.29. Traces of hydrochloric acid or of aluminum trichloride converted **73** (R = CH_3) to 2-(2-hydroxyethoxymethyl)benzaldehyde. ^{1}H NMR: δ 1.37 (br s, 1 H), 3.15-3.3 (m, 2 H), 3.4-3.55 (m, 2 H), 4.73 (s, 2 H), 6.95-7.25 (m, 3 H), 7.35-7.5 (m, 1 H), 9.92 (s, 1 H).

Photolysis of **69** in 0.2 M CF_3CH_2ONa-TFE afforded almost exclusively 2-[2-((2,2,2-trifluoroethoxy)methyl)phenyl]-1,3-dioxolane (**73**, R = CF_3CH_2). ^{1}H NMR: δ 3.84 (q, J = 8.6 Hz, 2 H), 3.95-4.15 (m, 4 H), 4.87 (s, 2 H), 6.00 (s, 1 H), 7.25-7.7 (m, 4 H). Anal. Calcd for $C_{12}H_{13}F_3O_3$: C, 54.96; H, 5.00. Found: C, 55.10; H, 5.06.

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The NEER Principle. Ground-State Conformational Bias in Triene Photocyclizations

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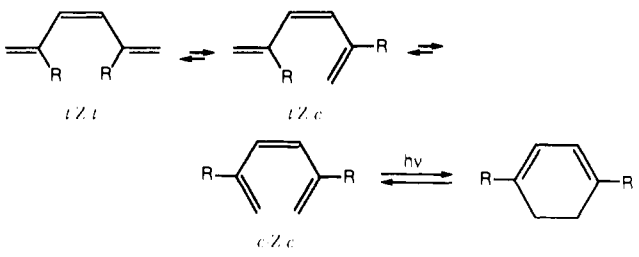
Abstract: A series of closely related trienes was transformed to cyclohexadienes by photocyclization. The diastereoselectivity observed for the series can be rationalized as the result of conformational bias in the ground states of the starting trienes. The results thereby lend experimental support to the Non-Equilibration of Excited Rotamers or NEER principle.

The fascinating subtleties involved in the photochemistry of vitamin D_3 has stimulated a high level of research in the light-induced transformations of simple, 1,3,5-hexatrienes and related systems.[1] A key concept has emerged from these combined studies that is applicable to the analysis of excited singlet states in general: the Non-Equilibration of Excited-state Rotamers, or NEER principle. First advanced by Havinga[2] to explain anomalies in vitamin D_3 photochemistry, it was latter extended to the analysis of the chemistry of simple hexatrienes[3] where it has its most fundamental application. In these systems, the yield of cyclohexadiene is increased by substituents at the 2- and 5-positions, consistent with the NEER principle that concludes that the various conformers of the excited singlet of the triene (*t-Z-t*, *c-Z-t*, *c-Z-c*) can not interconvert within the lifetime of that state (Scheme I).

Further studies by Dauben[4] confirmed the importance of the equilibrium, ground-state population of the *c-Z-c* conformer, as

Scheme I



t Z t *t Z c* *c Z c*

influenced by steric factors, on the cyclization to form cyclohexadiene products. In a related study, Baldwin[5] drew a correlation between the conformational bias in a cyclohexadiene and the stereochemistry of the triene cycloreversion product.

On the basis of these fundamental investigations, we devised a synthesis of the novel natural material ikarugamycin (**1**) in which one of the three separate, key concepts that we employed for stereochemical control is illustrated in Scheme II and involved the photoinduced closure of triene **2** to cyclohexadiene **3**. Critical to the control of stereochemistry at the new chiral centers at C-13 and C-14 was the concept inherent in the NEER principle that closure of the singlet photoexcited state of a triene would occur more rapidly than conformational changes. Indeed, it has been

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(2) Havinga, E.; Schlatmann, J. L. M. A. *Tetrahedron* **1961**, *16*, 146. Havinga, E. *Chimia* **1962**, *16*, 145. Jacobs, H. J. C.; Gielen, J. W. J.; Havinga, E. *Tetrahedron Lett.* **1981**, *22*, 4013.

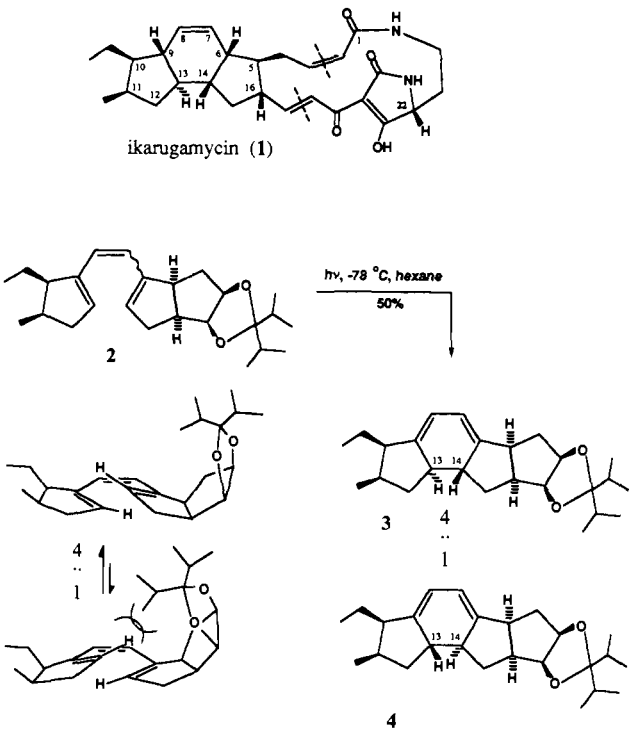
(3) Vroegop, P. J.; Lugtenburg, J.; Havinga, E. *Tetrahedron* **1973**, *29*, 1393.

(4) Dauben, W. G.; Rabinowitz, J.; Vietmeyer, N. D.; Wendschuh, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 4285.

(5) Baldwin, J. E.; Krueger, S. M. *J. Am. Chem. Soc.* **1969**, *91*, 6444.

0002-7863/89/1511-1473$01.50/0

Scheme II



suggested that conformational changes that involve disruption of the extended π system by rotation to orthogonality would force intersystem crossing to the triplet state that is known not to cyclize. In either case, the product composition would represent a "snapshot" of the conformational bias of the starting triene for one of the diastereomeric coils. In 1987 we reported[6] on the successful completion of our synthesis of the carbocyclic portion where moderate, synthetically significant 4:1 bias in the desired sense was indeed observed in the photochemical transformation.

Our prediction of a bias in favor of the desired diastereomer **3** was based on the idea that the ground-state coil of triene **2** that would lead to the undesired stereoisomer **4** would be disfavored by a significant steric interaction between the endo-oriented isopropyl group of the ketal and the indicated vinyl hydrogen. The observed bias of approximately 4:1 for the desired direction of cyclization was clearly the result of kinetic rather than thermodynamic control since extended photolysis after conversion was nearly complete led to a 1:1 mixture, presumably the result of equilibration achieved through photochemically induced reversal of the reaction. These results are certainly consistent with the NEER principle, and thus we felt compelled to test the unprecedented long-range stereochemical control factor that we had proposed.

Clearly, removal of the methyl groups from the ketal would be expected to eliminate the steric interaction and represented our first test since the appropriate triene could be accessed readily from the appropriate diol precursor to form the simple acetonide **5** (the general synthetic route for all the trienes is the same as that for **2**, described in detail in ref 6). However, cyclization of **5** (at −78 °C) provided stereochemical bias in the same direction and with approximately the same magnitude as observed with the original triene **2**. The observations with both **2** and **5** could be rationalized if the steric interaction in the disfavored coil is between some other part of the ketal moiety and the vinyl hydrogen. Thus, cyclization of the stereoisomer acetonide **8** was examined. While the bias was somewhat lower (2.5:1), the same diastereomeric arrangement observed with the previous two trienes was favored. Total removal of the annulated cyclopentane ring from the structure left a triene (**11**) where no substituent could interfere with the vinyl hydrogen yet the bias was again 4:1 in the same

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Scheme III

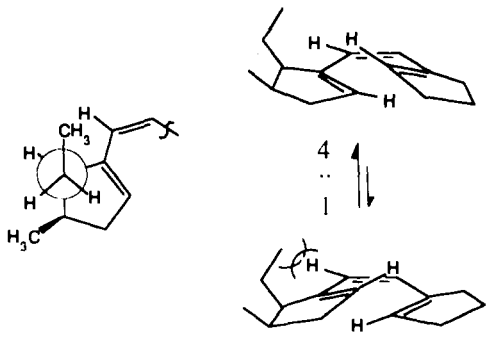

Table I

pair	shift effect, Δδ C-10	C-11	C-13
3 → **4**	−1.9	−2.3	+1.7
6 → **7**	−2.9	−2.4	+1.6
9 → **10**	−1.8	−2.4	+1.6
12 → **13**	−2.2	−2.4	+1.5
15 → **16**	−2.7	−2.0	+1.2

direction observed with **2** and **5**! Clearly, the origin of the bias must reside in the ethyl and methyl substituents since they are the only remaining groups that desymmetrize the triene (photolysis of the symmetric triene **17** resulted, of course, in a racemic mixture of **18** and **19**). Indeed, reversal of these two groups (triene **14**) removes the bias, resulting in a 1:1 mixture of the diastereomeric cyclohexadienes **15** and **16**.

In retrospect the origin of the bias is clear. The conformation of the ethyl group with its methyl oriented as shown in Scheme III is heavily favored, since in the other two rotamers this group experiences an unfavorable, δ steric interaction with the other methyl group. However, in this disposition, the methyl of the ethyl group will control the orientation about the C-8/C-9 σ bond so as to avoid steric interaction with both the vinyl hydrogen and C-7. Of the two coils that can lead directly to product, one involves a significantly greater separation of the hydrogen and the methyl group. Molecular mechanics calculations provide an energy difference between the two coils (for **11**) of 1 kcal/mol, in qualitative agreement with the magnitude of the bias observed.

In conclusion, this extended study of variously substituted trienes lends additional confirmation to the NEER principle in systems where product stabilities cannot be used, as they can in the vitamin D_3 field, to explain the stereochemical outcome.

Stereochemical Assignments. The stereochemistry at C-13 and C-14 in the major diastereomer (**3**) from photocyclization of **2** was unequivocally assigned by single-crystal, X-ray analysis of an intermediate further along in the synthetic pathway.[6] Assignment of stereochemistry for the major and minor cyclohexadiene products for all of the remaining reactions was carried out by carbon NMR spectral analysis on the mixture of diastereomers. Indeed, neither the starting trienes nor the product dienes are stable at room temperature, especially in contact with oxygen or light, and product analysis would have been exceptionally more complicated were it not for the consistent shift changes between the two diastereomers. We have extracted in Table I the shift effects for those carbons that are significantly affected (>1 ppm) by a change in stereochemistry from 13*R*,14*R* to 13*S*,14*S*.

Experimental Section

Reactions were routinely run under a dry nitrogen or argon atmosphere. Dichloromethane, methanesulfonyl chloride, pyridine, and triethylamine were distilled from calcium hydride and stored over 4A molecular sieves. Methanol was dried over 3A molecular sieves, benzene was dried over 4A molecular sieves, and acetone was dried over anhydrous copper sulfate. Skelly B (hexane) was stirred with concentrated sulfuric acid, neutralized with sodium carbonate, filtered through alumina, and distilled. Skelly B used for photolysis was more thoroughly purified by refluxing with sulfuric acid for 2 days before neutralization

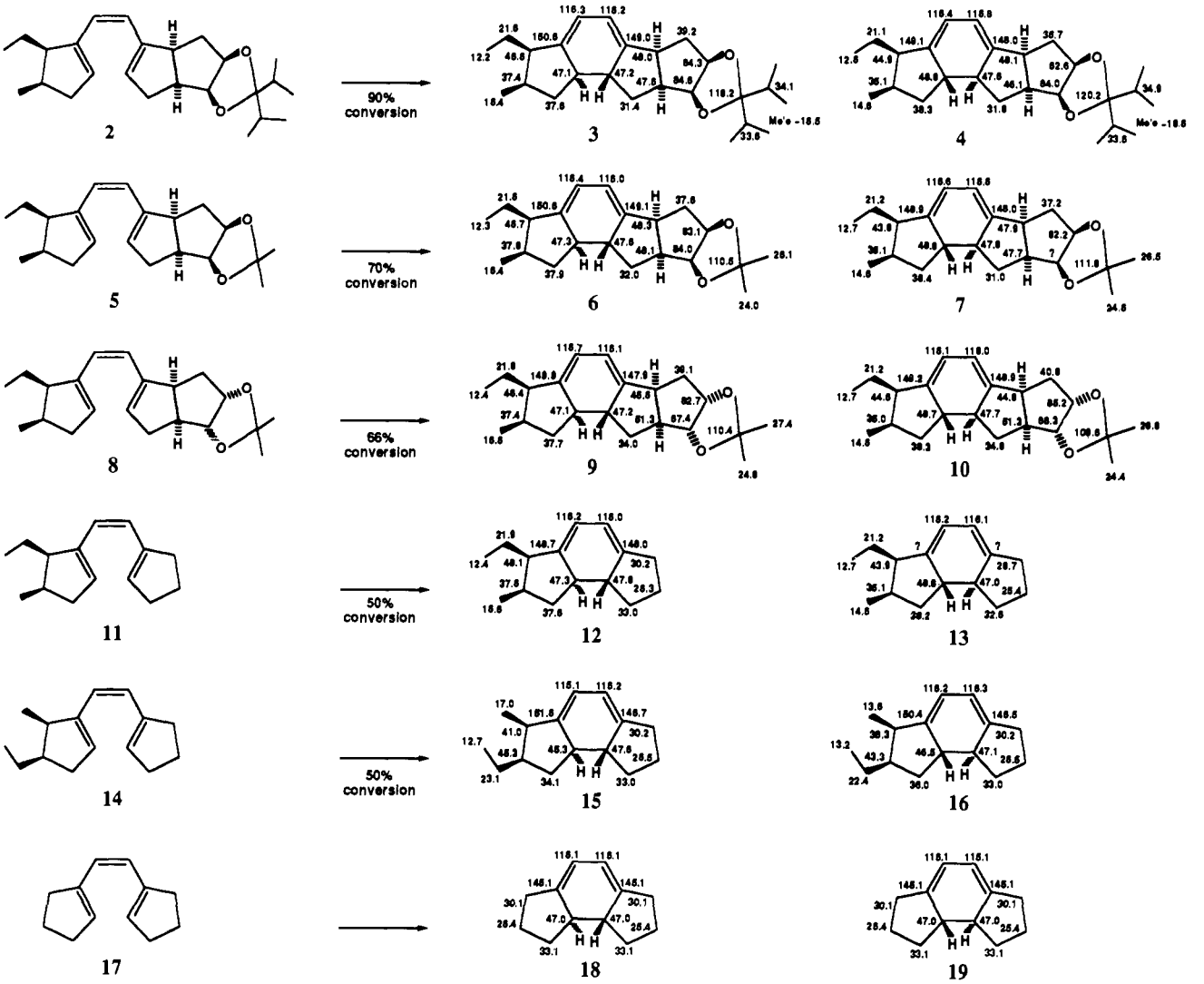

Figure 1. In all cases an approximately equal mixture of *cis* and *trans* trienes was used as *cis–trans* interconversion was observed to be significantly faster than photocyclization. Carbon-13 chemical shift assignments were made based on analogy with model systems with the aid of off-resonance decoupling. Assignments for similarly substituted carbons that differ by less than 1.0 δ may be reversed.

and distillation. Traces of oxygen were removed immediately before use by bubbling argon through the solvent for at least 1 h. All other solvents and reagents were reagent grade and used as received unless stated otherwise. Brine refers to a saturated aqueous solution of sodium chloride. Organic solutions were dried over 4A molecular sieves before solvent removal on a rotary evaporator and high-vacuum drying (for nonvolatile samples). HPLC separations were performed on normal-phase silica columns with refractive index detection using Waters 6000A analytical pump or Prep 500 preparative system. UV spectra were obtained as hexane solutions on a Cary 14 spectrophotometer. NMR spectra were obtained with Varian FT-80A, Varian HA-100, Nicolet NT-360, and General Electric QE-300 spectrometers, in deuteriochloroform referenced to internal TMS. ^{13}CMR assignments were confirmed by off-resonance decoupling where appropriate. For consistency, spectral assignments for all compounds follow the numbering used for ikarugamycin (**1**).

All of the trienes were prepared by Wittig reactions analogous to that described in detail for **2** in ref 6 and were obtained as cis:trans mixtures. Only their spectra are given here. Photolyses were also carried out as described.[6] The aldehyde for **11**, **14**, and **17** was known[7] as was the phosphorane for **17**.[8] **17** itself has also been prepared by a different route.[1b]

Methyl (1*S*)-*cis*,*endo*-6,7-Dihydroxy-*cis*-bicyclo[3.3.0]oct-2-ene-2-carboxylate Acetonide. A solution of 1.8 g (9.2 mmol) of the corresponding endo diol[6] and 0.18 g (0.9 mmol, 0.1 equiv) of *p*-toluenesulfonic acid monohydrate in 18 mL of acetone was stirred overnight at room temperature. Sodium bicarbonate (0.09 g, 1 mmol) was added, and after 15 min more, the mixture was filtered through silica gel with acetone. Concentration provided 2.1 g (97%) of the crude acetonide, which was used without further purification: ^{13}CMR (20 MHz) δ 165.7 (s, C7), 143.7 (d, C14), 138.1 (s, C6), 110.5 (s, CMe_2), 82.5 (d, C17 or C3), 82.1 (d, C3 or C17), 51.2 (q, OMe), 50.9 (d, C5), 45.6 (d, C16), 34.0 (t, C4), 32.1 (t, C15), 26.0 (q, exo Me), 24.4 (q, endo Me).

(1*S*)-*cis*,*endo*-6,7-Dihydroxy-*cis*-bicyclo[3.3.0]oct-2-ene-2-methanol Acetonide. Diisobutylaluminum hydride (45 mL of 0.6 M solution in hexane, 27 mmol, 3 equiv) was added dropwise over 25 min to a stirred solution of 2.1 g (9 mmol) of the above crude acetonide methyl ester in 30 mL of dichloromethane cooled to −78 °C. The solution was stirred 45 min more at −78 °C and then for 1 h at 0 °C. Methanol (5 mL) was added dropwise, and stirring was continued 15 min more at 0 °C before 7 mL of 10% w/w KOH was added. After being warmed to room temperature, the mixture was partioned between ether and brine. Concentration of the organic layers provided 1.8 g (97%) of crude alcohol which was used without further purification: ^{13}CMR (20 MHz) δ 144.5 (s, C6), 127.1 (d, C14), 110.5 (s, CMe_2), 82.8 (d, C17 or C3), 82.3 (d, C3 or C17), 60.4 (t, C7), 51.7 (d, C5), 46.0 (d, C16), 32.5 (t, C4), 31.1 (t, C15), 25.9 (q, exo Me), 24.4 (q, endo Me).

(1*S*)-*cis*,*endo*-6,7-Dihydroxy-*cis*-bicyclo[3.3.0]oct-2-ene-2-carboxaldehyde Acetonide. Pyridinium dichromate[9] (10 g, 27 mmol, 3 equiv) was added rapidly to a stirred solution of 1.8 g (9 mmol) of the above crude acetonide alcohol in 18 mL of dichloromethane. After 8 h at room temperature, the mixture was filtered through silica gel with ether. Concentration of the filtrate provided 1.2 g (65%) of crude aldehyde required for **5** which was purified by preparative HPLC using 3:1 Skelly

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(8) Monti, S. A.; McAninch, T. W. *Tetrahedron Lett.* **1974**, 3239.
(9) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

B/ethyl acetate: ^{13}CMR (20 MHz) δ 189.4 (C7), 152.6 (C14), 148.9 (C6), 110.2 (CMe_2), 82.7 (C17 or C3), 81.9 (C3 or C17), 48.8 (C5), 45.7 (C16), 33.0 (C15 or C4), 32.8 (C4 or C15), 26.1 (exo Me), 24.2 (endo Me).

Endo acetonide triene 5: (NMR data for *cis* isomer only) ^{1}HMR (360 MHz) δ 5.98 (d, 1 H, J = 12.2, H7 or H8), 5.86 (d, 1 H, J = 12.2, H8 or H7), 5.58 (nm, 1 H, H13 or H14), 5.53 (nm, 1 H, H14 or H13), 4.62 (td, 1 H, J = 5.8 1.6, H3), 4.53 (dd, 1 H, J = 7.7, 5.9, H17), 3.42 (br t, 1 H, H5), 2.65 (m, 2 H), 2.56 (nm,1 H, H10 or H16), 2.38 (m, 3 H), 1.95 (br d, 1 H, J = 14.8, H4), 1.70 (dddd, 1 H, J = 14.6, 8.7, 5.8, 0.5, H4), 1.43 (m, 3 H, H11 + CH_2 of Et), 1.31 (s, 3 H, acetonide Me), 1.25 (s, 3 H, acetonide Me), 0.98 (d, 3 H, J = 6.8, 11-Me), 0.86 (t, 3 H, J = 7.4, Me of Et); ^{13}CMR (90 MHz) δ 144.7 (s, C9), 143.3 (s, C6), 131.1 (d, C7 or C8), 130.0 (d, C8 or C7), 125.5 (d, C13 or C14), 125.1 (d, C14 or C13), 110.5 (s, CMe_2), 82.9 (d, C17 or C3), 82.8 (d, C3 or C17), 52.0 (d, C10), 50.8 (d, C5), 45.6 (d, C16), 40.0 (t, C12), 36.5 (d, C11), 33.5 (t, C4), 31.4 (t, C15), 26.3 (q, exo acetonide Me), 24.7 (q, endo acetonide Me), 20.5 (t, CH_2 of Et), 15.3 (q, 11-Me), 12.5 (q, Me of Et).

(1*S*)-*cis*,*exo*-6,7-Dihydroxy-*cis*-bicyclo[3.3.0]oct-2-ene-2-carboxaldehyde Acetonide. The corresponding exo diol[6] was treated exactly as in the three steps above to give in 60% overall yield the exo acetonide aldehyde required for **8**: ^{13}CMR (90 MHz) δ 189.2 (d, C7), 150.7 (nd, C6), 149.9 (d, C14), 110.6 (s, CMe_2), 87.1 (d, C17), 83.2 (d, C3), 50.4 (d, C16), 46.1 (d, C5), 37.3 (t, C15 or C4), 37.1 (t, C4 or C15), 27.5 (q, exo Me), 25.0 (q, endo Me).

Exo acetonide triene 8: ^{13}CMR (90 MHz) *cis* δ 145.2 (C9 or C6), 144.1 (C6 or C9), 129.8 (C7 or C8), 129.2 (C8 or C7), 126.6 (C13), 124.8 (C14), 110.4 (CMe_2), 88.3 (C17), 82.7 (C3), 51.2 (C10), 50.3 (C16 or C5), 49.8 (C5 or C16), 40.0 (C12), 37.2 (C4), 36.3 (C15 or C11), 36.2 (C11 or C15), 27.7 (exo acetonide Me), 25.1 (endo acetonide Me), 20.7 (CH_2 of Et), 15.4 (11-Me), 12.5 (Me of Et); *trans* δ 147.2 (C9 or C6), 147.1 (C6 or C9), 128.5 (C8 or C7), 128.4 (C7 or C8), 126.7 C13), 124.5 (C14), 110.1 (CMe_2), 86.8 (C17), 83.8 (C3), 51.3 (C16), 47.7 (C5), 47.2 (C10), 39.9 (C12), 38.2 (C11 or C4), 38.1 (C4 or C11), 36.4 (C15), 27.4 (exo acetonide Me), 24.9 (endo acetonide Me), 21.0 (CH_2 of Et), 15.2 (11-Me), 12.3 (Me of Et).

Triene 11: ^{13}CMR (90 MHz) *cis* δ 144.5 (s, C9), 142.6 (s, C6), 132.7 (d, C7), 129.9 (d, C8), 126.0 (d, C13 or C14), 125.9 (d, C14 or C13), 52.1 (d, C10), 40.1 (t, C12), 36.0 (d, C11), 34.3 (t, C5), 32.2 (t, C15), 24.3 (t, C16), 21.0 (t, CH_2 of Et), 15.5 (q, 11-Me), 12.8 (q, Me of Et); *trans* δ 147.4 (s, C9), 143.3 (s, C6), 130.3 (d, C7), 128.9 (d, C8), 126.5 (d, C13), 125.6 (d, C14), 47.2 (d, C10), 39.9 (t, C12), 38.3 (d, C11), 33.0 (t, C5), 31.3 (t, C15), 23.3 (t, C16), 21.1 (t, CH_2 of Et), 15.3 (q, 11-Me), 12.3 (q, Me of Et).

Methyl *cis*-7,8-Dihydroxy-*cis*-bicyclo[3.3.0]oct-2-ene-2-carboxylate. Woodward oxidation of the methyl ester of *cis*-bicyclo[3.3.0]octa-2,7-diene-2-carboxylic acid[10] was carried out in 85% yield exactly as described for the 2,6-diene isomer.[6] A 4:1 mixture of endo:exo *cis*-diols was obtained and this was cleaved directly in the next step without separation: ^{13}CMR (20 MHz) endo δ 166.5 (s, C8), 145.2 (d, C13), 134.4 (s, C9), 75.2 (d), 73.2 (d), 52.8 (d, C10), 51.6 (q, OMe), 41.1 (t, C12), 38.4 (t), 36.9 (d, C11); exo δ 166.1 (s, C8), 144.1 (d, C13), 136.4 (s, C9), 78.5 (d), 73.8 (d), 56.2 (d, C10), 51.6 (q, OMe), 40.4 (t, C12), 38.8 (t), 37.7 (d, C11).

Methyl *cis*-4-Ethyl-5-methyl-1-cyclopentene-1-carboxylate. Periodate cleavage of the above diol mixture, borohydride reduction of the resultant dialdehyde, mesylation, and zinc reduction were carried out in 60% overall yield exactly as described for the 5-ethyl-4-methyl isomer:[6] ^{13}CMR (20 MHz) δ 165.2 (s, C8), 142.5 (s, C9), 142.3 (d, C13), 51.0 (q, OMe), 45.1 (d, C11), 40.2 (d, C10), 36.9 (t, C12), 23.3 (t, CH_2 of Et), 13.0 (q, 10-Me + Me of Et).

***cis*-4-Ethyl-5-methyl-1-cyclopentene-1-methanol.** DIBAH reduction of the above ester was carried out in 80% yield exactly as described for the 5-ethyl-4-methyl isomer:[6] ^{13}CMR (20 MHz) δ 150.3 (C9), 123.7 (C13), 60.5 (C8), 45.6 (C11), 40.9 (C10), 36.2 (C12), 23.5 (CH_2 of Et), 13.2 (Me of Et), 12.7 (10-Me).

***cis*-1-(Bromoethyl)-4-ethyl-5-methylcyclopentene.** The above alcohol was converted to the bromide in 74% yield by using PBr_3 exactly as described for the 5-ethyl-4-methyl isomer:[6] ^{13}CMR (20 MHz) δ 146.4 (s, C9), 129.5 (d, C13), 45.6 (d, C11), 41.6 (d, C10), 36.8 (t, C12), 30.4 (t, C8), 23.8 (t, CH_2 of Et), 13.4 (q, Me of Et), 12.8 (q, 10-Me).

[(*cis*-4-Ethyl-5-methyl-1-cyclopenten-1-yl)methyl]triphenylphosphonium Bromide. Conversion of the above bromide into the phosphonium salt required for **14** was carried out in 78% yield as described for the 5-ethyl-4-methyl isomer,[6] except that the reaction was stirred for only 5 days: ^{13}CMR (20 MHz) δ 135.8 (ds, J_{PC} = 9.4, C9), 135.1 (dd, J_{PC} = 3.0, *p*-Ar), 134.1 (dd, J_{PC} = 10.3, C13), 133.9 (dd, J_{PC} = 9.9, *o*-Ar), 130.3 (dd, J_{PC} = 12.6, *m*-Ar), 118.5 (ds, J_{PC} = 85.5, *i*-Ar), 44.4 (sd, C11), 44.0 (dd, J_{PC} = 2.9, C10), 36.4 (dt, J_{PC} = 2.6, C12), 25.1 (dt, J_{PC} = 50.0, C8), 23.0 (st, CH_2 of Et), 12.8 (sq, Me of Et), 12.1 (dq, J_{PC} = 2.9, 10-Me).

Triene 14: ^{13}CMR (75 Mzh) *cis* δ 147.0 (s, C9), 142.5 (s, C6), 132.5 (d, C7), 128.8 (d, C8), 125.5 (d, C13 or C14), 125.4 (d, C14 or C13), 44.9 (d, C11 or C10), 44.0 (d, C10 or C11), 36.8 (t, C12), 34.4 (t, C5), 32.3 (t, C15), 24.4 (t, C16), 23.3 (t, CH_2 of Et), 13.1 (q, Me of Et or 10-Me), 12.9 (q, 10-Me or Me of Et); *trans* δ 149.6 (s, C9), 143.3 (s, C6), 130.3 (d, C7), 128.2 (d, C8), 126.7 (d, C13), 125.1 (d, C14), 45.9 (d, C11), 39.6 (d, C10), 36.5 (t, C12), 33.1 (t, C5), 31.3 (t, C15), 23.5 (t, CH_2 of Et or C16), 23.3 (t, C16 or CH_2 of Et), 13.1 (q, Me of Et), 12.7 (q, 10-Me).

Triene 17: UV, *cis* 250 (br) nm, *trans* 261.5, 272, 284 nm; ^{1}HMR (100 MHz) *cis* δ 5.95 (br s, 2 H, H7,8), 5.62 (br s, 2 H, H13,14), 2.38 (br t, 8 H, J = 6.6, H5,10,12,15), 1.86 (br pentet, 4 H, J = 6.8, H11,16); *trans* δ 6.33 (s, 2 H, H7,8), 5.72 (br s, 2 H, H13,14), 2.45 (br t, 8 H, J = 6.8, H5,10,12,15), 1.91 (br pentet, 4 H, J = 7.2, H11,16); ^{13}CMR (20 MHz) *cis* δ 142.0 (C6,9), 131.4 (C7,8) 126.0 (C13,14), 35.3 (C5,10), 32.6 (C12,15), 24.2 (C11,16); *trans* δ 143.2 (C6,9), 130.5 (C7,8), 126.1 (C13,14), 33.1 (C5,10), 31.3 (C12,15), 23.3 (C11,16).

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