Cyclopentannulation by an Iterative Process of Sequential Claisen Rearrangement and Enyne Radical Closure: Routes to Triquinane and Propellane Systems and Use in the Synthesis of (±)-Ceratopicanol

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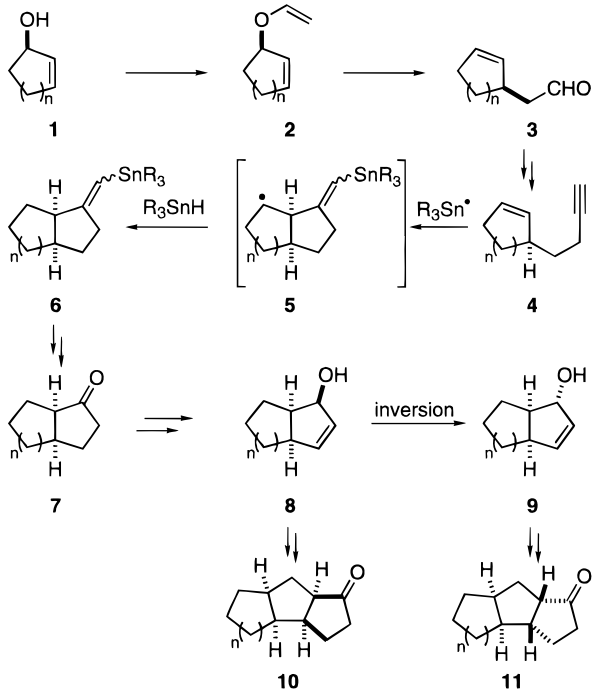
Cycloalkenyl acetylenes **4**, which are easily prepared from allylic alcohols by Claisen rearrangement and homologation (**1** → **4**), generally undergo radical cyclization (**4** → **6**) on treatment with stannyl radicals. The products (**6**) can themselves be converted into allylic alcohols, so that the annulation sequence can then be repeated. In certain cases enyne cyclization initiated by stannyl radicals does not work, but an alternative process (*cf.* Scheme 9) of epoxide opening with bis(cyclopentadienyl)titanium(III) chloride can then be used. Di- and triquinanes (Scheme 3) were made by the stannyl radical approach; the epoxide route was used to prepare a simple propellane (Scheme 4) and in a synthesis of (±)-ceratopicanol (Schemes 5 and 9).

We report a procedure for fusing a five-membered ring onto a cyclic allylic alcohol.[1] The method, which is an iterative one, has been used to construct members of the triquinane class; a slight modification gave a propellane, and the modified procedure was used to synthesize the sesquiterpene (±)-ceratopicanol.

The principle of our method is summarized in Scheme 1. An allylic alcohol (**1**) can be converted by Claisen rearrangement (**1** → **2** → **3**) and then by homologation (**3** → **4**) into an enyne in which the acetylenic chain is on the same face as the original hydroxyl. Treatment with stannyl radicals gives a vinyl stannane (**4** → **5** → **6**), which is convertible into a ketone (**6** → **7**). Since ketones may be easily desaturated and reduced, compounds of type **7** are synthetically equivalent to allylic alcohols **8**. Stereochemical inversion would serve to convert **8** into its epimer **9**. Both **8** and **9** are members of the allylic alcohol class used to begin the sequence, so that, in principle, repetition of the whole process would result in annulation of an additional ring on the same face as the new hydroxyl. There is also the possibility of subjecting allylic alcohols **8** and **9** to 1,3-transposition[2] so as to fuse the next ring on a different edge of the substrate.

We initially sought to implement this plan along the lines shown in Scheme 2, but found that homologation of **16** was difficult, as both the derived tosylate and bromide were inert to displacement by lithium acetylide under several different conditions. Presumably, this low reactivity is due to the electron-withdrawing methoxy substituent, whose purpose was to facilitate formation of a 2,3-double bond in **18**. In any event, we did not pursue the matter, as we quickly found another route (Scheme 3), in which the 2,3-double bond is formed by standard methods for ketone desaturation.

Scheme 1



Diol **19** was monosilylated (**19** → **20**) and the resulting alcohol subjected to Mitsunobu inversion (**20** → **21** → **22**), each step giving the expected product in at least 90% yield. Formation of the vinyl ether **23**, by treatment with ethyl vinyl ether in the presence of mercuric acetate[3] (99%) and thermolysis (200 °C), then gave aldehyde **24** (90%). In this series, the purpose of the *t*-$BuMe_2SiO$ group is simply to raise the molecular weight of early intermediates so that product isolation is simplified, and the reason for using the inverted alcohol **22** rather than the initial alcohol **20** is that preliminary experiments on the Claisen rearrangement step (*cf.* **23** → **24**) did not work with material derived from **20**.[4]

From **24**, the required homologation to enyne **27** was easily achieved by reduction ($LiAlH_4$, 89%), replacement

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(1) Preliminary communications: (a) Clive, D. L. J.; Manning, H. W. *J. Chem. Soc., Chem. Commun.* **1993**, 666. (b) Clive, D. L. J.; Magnuson, S. R. *Tetrahedron Lett.* **1995**, *36*, 15.

(2) *Cf.* (a) Wharton, P. S.; Bohlen, D. H. *J. Org. Chem.* **1961**, *26*, 3615. (b) Dupuy, C.; Luche, J. L. *Tetrahedron* **1989**, *45*, 3437. (c) Discordia, R. P.; Murphy, C. K.; Dittmer, D. C. *Tetrahedron Lett.* **1990**, *31*, 5603. (d) Liotta, D.; Zima, G.; Saindane, M. *J. Org. Chem.* **1982**, *47*, 1258. (e) Barton, D. H. R.; Hay Motherwell, R. S.; Motherwell, W. B. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2363. (f) Yasuda, A.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1757. (g) Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682.

(3) Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2828.

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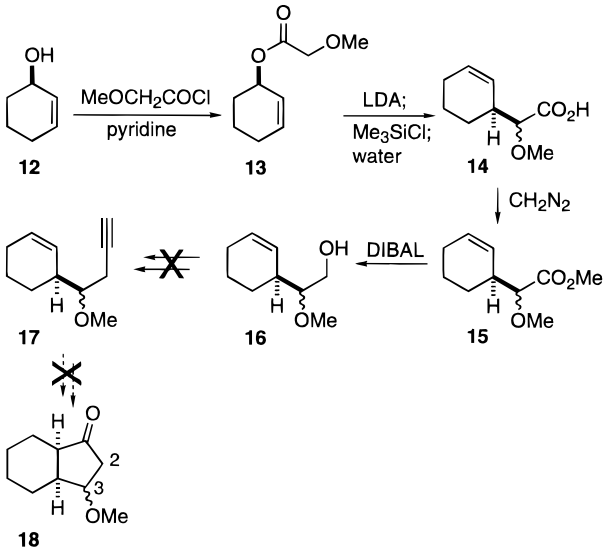
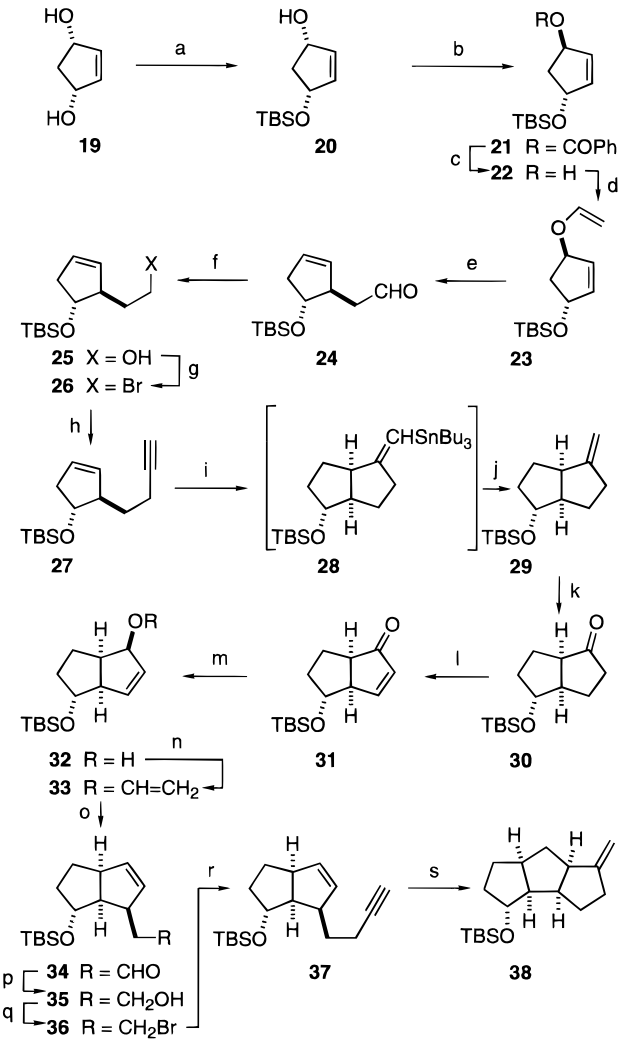
Scheme 2[a]



[a] All compounds are racemic.

Scheme 3[a]



[a] TBS = *t*-BuMe$_2$Si. Key: (a) NaH, *t*-BuMe$_2$SiCl, 96%; (b) Ph$_3$P, PhCOOH, DEAD, 97%; (c) LiAlH$_4$, 94%; (d) Hg(OAc)$_2$, ethyl vinyl ether, 99%; (e) 200 °C, 90%; (f) LiAlH$_4$, 89%; (g) Ph$_3$P, CBr$_4$, 96%; (h) lithium acetylide, THF, HMPA, 89%; (i) Bu$_3$SnH, Et$_3$B, air, (j) silica, 85% from **27**; (k) OsO$_4$, NMO, 99%; Pb(OAc)$_2$, K$_2$CO$_3$, 93%; (l) LDA, PhSSPh; MCPBA, 73%; (m) NaBH$_4$, CeCl$_3$·7H$_2$O, 91%; (n) NaOAc, Hg(OAc)$_2$, methyl vinyl ether, 72%; (o) *i*-Bu$_3$Al; (p) in situ reduction by *i*-Bu$_3$Al, 95% from **33**; (q) Ph$_3$P, CBr$_4$, 96%; (r) lithium acetylide, THF, HMPA, 93%; (s) Bu$_3$SnH, AIBN, PhMe, reflux, 79%.

of the resulting hydroxyl group by bromine (Ph$_3$P/CBr$_4$;[6] 96%), and nucleophilic displacement (89% yield) with lithium acetylide (**24** → **25** → **26** → **27**). Treatment of **27** with Bu$_3$SnH in the presence of Et$_3$B and air[7] then served to generate the cyclization product **28**.[8] This suffered protodestannylation[9] during flash chromatography, so that olefin **29** was isolated directly from this experiment (76%; 85% after correction for recovered **27**).

In order to prepare for the second iteration of the whole process, the double bond in **29** was cleaved, and this was best done by two standard steps: vicinal dihydroxylation with OsO$_4$[10] followed by glycol cleavage with Pb(OAc)$_4$.[11] The Lemieux−Johnson procedure[12] for double bond cleavage was also tried, but in this particular case, better yields (92% overall) are obtained by the two-step method. We had anticipated that standard selenoxide fragmentation would then lead to the unsaturated ketone **31**, but phenylselenenylation of **30** was very troublesome and inefficient. Oxidation of the triethylsilyl enol ether derived from **30** (LDA; Et$_3$SiCl), using Pd(OAc)$_2$,[13] gave enone **31** in 42% yield (from the enol ether). Fortunately, benzenesulfenylation of **30** proceeded smoothly,[14] and oxidation with *m*-CPBA, followed by thermolysis in refluxing decalin, converted **30** satisfactorily into **31** (73% overall). Reduction of the enone by NaBH$_4$ in the presence of CeCl$_3$·6H$_2$O gave, as expected, allylic alcohol **32** (91%) having the hydroxyl *endo* to the convex bicyclic system.

With **32** in hand, we had a choice of proceeding directly with a second annulation or first inverting the stereochemistry of the hydroxyl. We decided to preserve the stereochemistry of **32** since annulation would then have to occur on the more hindered face of the substrate and might therefore be a somewhat more demanding test than annulation on the other face. Accordingly, alcohol **32** was converted into its vinyl ether **33**. The hydroxyl in **32** proved to be decidedly hindered, and vinylation in the presence of ethyl vinyl ether and Hg(OAc)$_2$ was very slow. However, by using a long reaction time (48 h as compared with 18 h for **22**) and a reaction medium buffered by sodium acetate,[3] it was possible to isolate the required vinyl ether **32** in 91% yield (*cf.* 99% for **23**).

(4) Only a superficial study of thermal methods was made with the series from **20**, using a sulfoxide-based approach (*cf.* ref 5) or the mercuric ion mediated vinylation employed successfully for **22** → **23** → **24** (*cf.* ref 3). We did not establish whether Claisen rearrangement catalyzed by *i*-Bu$_3$Al, as used with **33**, would work in the series from **20**.

(5) Mandai, T.; Ueda, M.; Hasegawa, S.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 4041.

(6) Downie, I. M.; Holmes, J. B.; Lee, J. B. *Chem. Ind. (London)* **1966**, 900.

(7) (a) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. (b) Nozaki, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3465. (c) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 6127. (d) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron* **1989**, *45*, 923. (e) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1990**, *31*, 4681.

(8) We did not establish if the material is a mixture of both *Z* and *E* isomers or is just one isomer.

(9) *Cf.* Stork, G.; Mook, R. *J. Am. Chem. Soc.* **1987**, *109*, 2829.

(10) (a) Schröder, M. *Chem. Rev.* **1980,** *80*, 187. (b) VanRheenen, V.; Kelly, R. C., Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.

(11) Criegee, R.; Höger, E.; Huber, G.; Kruck, P.; Marktscheffel, F.; Schellenberger, A. *Ann.* **1956,** *599*, 81.

(12) Pappo, R.; Allen, D. S., Jr.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem.* **1956,** *21*, 478.

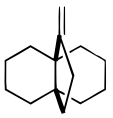
(13) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978,** *43*, 1011.

(14) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

Claisen rearrangement of **33** was expected to be troublesome, after the problems experienced in its preparation; in the event, extensive decomposition occurred under the conditions (refluxing decalin) that had been very successful with the simpler vinyl ether **23**. However, a fine alternative to thermal Claisen rearrangement is available in the form of catalysis by aluminum alkyls,[15] and in fact, when **33** was treated with *i*-Bu_3Al[16] at −78 °C, alcohol **35**—the result of rearrangement (**33** → **34**) and *in situ* reduction—was isolated in well over 90% yield. Bromide **36** was next prepared, and the halogen was displaced with lithium acetylide to afford enyne **37** in 89% overall yield from **35**. The enyne seemed to be inert to the conditions used previously for cyclization of **27**, but when the reaction was initiated with AIBN in refluxing toluene, the triquinane **38** was isolated in 79% yield, after destannylation on silica gel.

Formation of **38** took the route to a point where it overlaps with a compound type used in an earlier step (*cf.* **29**), and so we next tried to extend the method to the preparation of propellanes.[17]

Accordingly, enone **39**[18] was reduced (92%), and the resulting alcohol was converted into aldehyde **42** (Scheme 4). This was best achieved[19] (60% yield) by condensation with phenyl vinyl sulfoxide[5] (**40** → **41**) followed by thermolysis (5 days at 180 °C) (**41** → **42**). From this point, reduction (**42** → **43**; 92%), replacement of the hydroxyl by bromine (**43** → **44**; 92%), bromide displacement with lithium (trimethylsilyl)acetylide, and desilylation gave **45** (78% overall), the substrate for radical closure. When this compound was treated with Ph_3SnH and AIBN in refluxing benzene, three inseparable products were obtained, after destannylation on silica gel. We suspect, on the basis of ^{13}C NMR measurements, that the structures correspond to **46** and **47**, but the topic was



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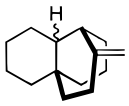

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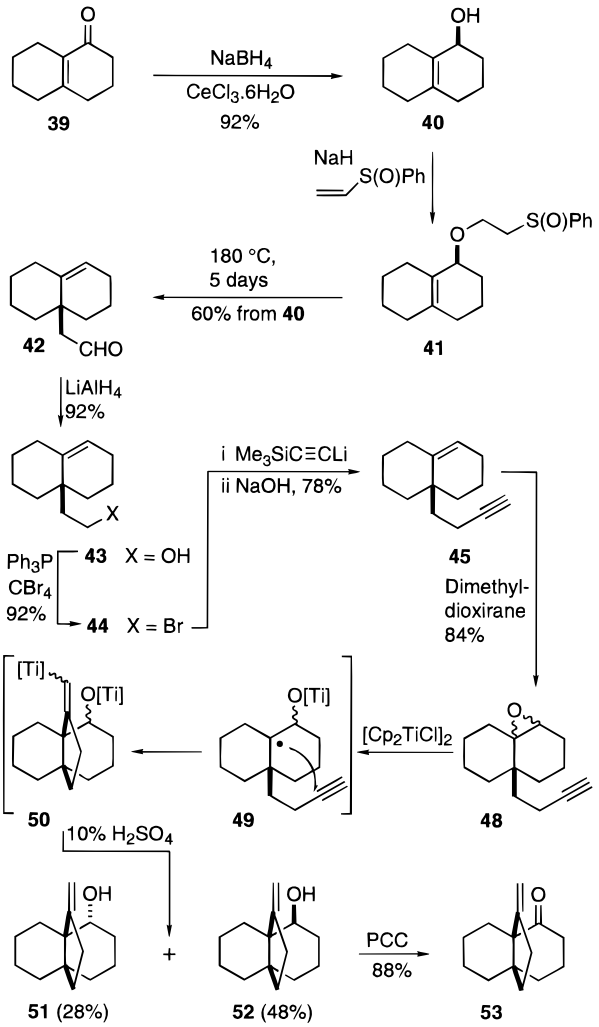
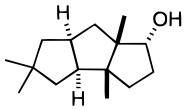
not pursued because related work on ceratopicanol (see later) had suggested an alternative method for radical closure of our enynes. Epoxidation of **45** with dimethyldioxirane gave **48** as a mixture of stereoisomers (84%), and when this material was treated with bis(cyclopentadienyl)titanium(III) chloride,[20] the desired products of radical cyclization, **51** (28%) and **52** (48%) (tentative stereochemical assignments, see the Experimental Section) were easily obtained via the presumed intermediates **49** and **50**. The alcohols could be separated, but the mixture was also oxidized directly (88%) to a single ketone (**53**).

Scheme 4



With the above experiments, especially those of Scheme 3, as background, we next sought to apply the tandem Claisen rearrangement/enyne radical closure to the synthesis of (±)-ceratopicanol **54**,[21] a substance that we thought would be readily accessible by this methodology.



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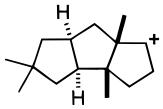

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The isolation[22] of ceratopicanol is of interest in the context of biogenetic theory, as the structure represents evidence for generation *in vivo* of carbonium ion **55**, a species suggested[23] to be a precursor to hirsutene and related natural products.

Our synthesis of racemic ceratopicanol begins with the known enone **56**,[24] which was reduced (**56** → **57**, DIBAL-H, 89%, Scheme 5) and then subjected to conditions of Mitsunobu inversion. This inversion process proved to be somewhat troublesome and, of several procedures that

(15) (a) Takai, K.; Mori, I.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 3985. (b) *Cf.* Nonoshita, K.; Maruoka, K.; Yamamoto, H.; *Bull. Chem. Soc. Jpn.* **1992**, *65*, 541. (c) For palladium catalysis, see, for example: Sugiura, M.; Yanagisawa, M.; Nakai, T. *Synlett* **1995**, 447.

(16) Paquette, L. A.; Friedrich, D.; Rogers, R. D. *J. Org. Chem.* **1991**, *56*, 3841.

(17) Review on propellanes: Ginsberg, D. *Top. Curr. Chem.* **1987**, *137*, 1.

(18) Rae, I. D.; Umbrasas, B. N. *Aust. J. Chem.* **1975**, *28*, 2669.

(19) Reaction of alcohol **40** with ethyl vinyl ether/$Hg(OAc)_2$ was very slow, and the yield varied from run to run; therefore, the sulfoxide route was examined.

(20) *Cf.* RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986.

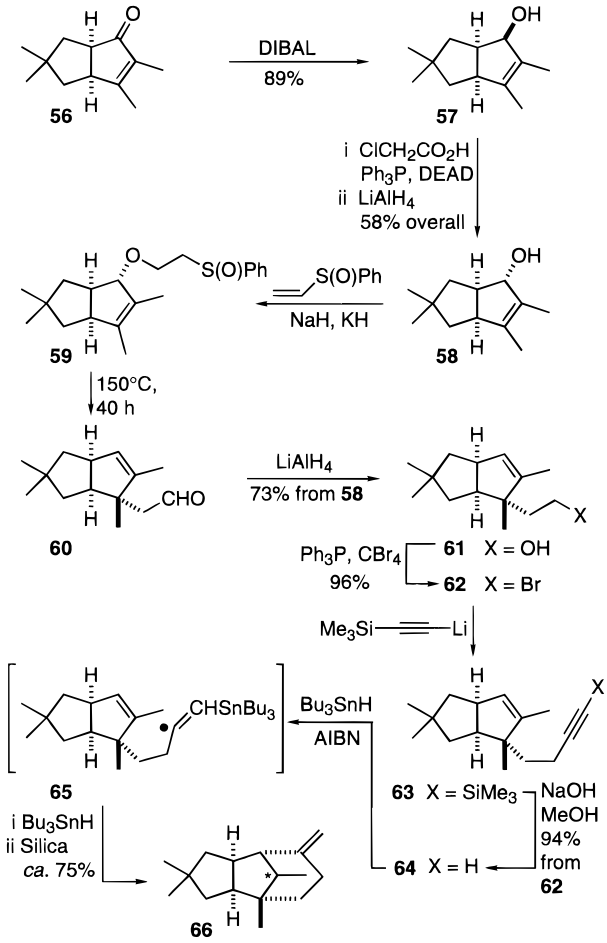
(21) For synthesis of the unnatural antipode, see: Mehta, G.; Karra, S. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1367.

(22) Hanssen, H.-P.; Abraham, W.-R. *Tetrahedron* **1988**, *44*, 2175.

(23) (a) Hayano, K.; Ohfune, Y.; Shirahama, H.; Matsumoto, T. *Helv. Chim. Acta* **1981**, *64*, 1347. (b) Comer, F. W.; McCapra, F.; Qureshi, I. H.; Scott, A. I. *Tetrahedron* **1967**, *23*, 4761.

(24) Tobe, Y.; Yamashita, D.; Takahashi, T.; Inata, M.; Sato, J.; Kakiuchi, K.; Kobiro, K.; Odaira, Y. *J. Am. Chem. Soc.* **1990**, *112*, 775 and references cited therein.

Scheme 5

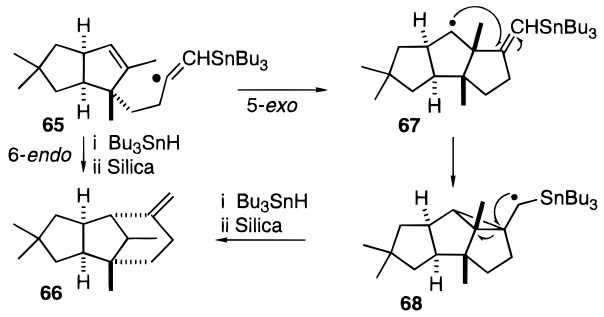


we tried,[25] only the use of chloroacetic[26] acid, followed by reduction ($LiAlH_4$), gave an acceptable result (58% overall). As in our earlier studies (Schemes 3 and 4), *exo* alcohol **58** was next converted into the derived vinyl enol ether and then into the product of Claisen rearrangement and reduction (**61**). These modifications could be accomplished by exchange with ethyl vinyl ether and catalyzed (*i*-Bu_3Al) rearrangement, followed by *in situ* reduction, but were more reliably done (73% overall) by addition to phenyl vinyl sulfoxide, thermal rearrangement (150 °C), and reduction ($LiAlH_4$) (**58** → **59** → **60** → **61**). Alcohol **61** was converted efficiently (96%) into the corresponding bromide (**62**), again using Ph_3P/CBr_4, and the halogen was displaced with lithium (trimethylsilyl)-acetylide. Desilylation with methanolic sodium hydroxide then gave the key enyne **64** in excellent overall yield (94% from bromide **62**).

When the enyne was treated with Bu_3SnH (0.01−0.07 M) in refluxing benzene, with AIBN as an initiator, only alkene **66** was isolated after exposure to silica gel (for protodestannylation). The compound was a single stereoisomer, but the relative stereochemistry at the starred atom was not established.

Formation of **66** could occur either by direct 6-*endo* closure, or by the normal 5-*exo* pathway (**65** → **67**) (Scheme 6), as observed in our model studies (see Scheme 3), followed by rearrangement[27] (**67** → **68** → **66**). If the

Scheme 6



rate of bimolecular hydrogen abstraction from stannane by the hindered radical **67** is slow, rearrangement of **67** to **66** need not be unusually fast; however, we were unable to rule out the possibility that formation of **66** is an example of kinetically preferred direct 6-*endo* closure.[28] For example, use of a higher stannane concentration (1.1 M) still gave **66** (and not the desired compound), as well as hydrostannylation products of the triple bond and, when we did the experiment in the presence[29] of a trace of PhSeSePh—in the hope of trapping **67**—the outcome was unchanged.

It is not clear why anomalous behavior is observed in this case, since several examples are known in which vinyl radicals cyclize onto proximally substituted nonconjugated double bonds,[9,30] but in any event, we were forced to modify the approach, and we now tried to generate the radical at a different position so that closure would occur *onto* the triple bond.

Alcohol **61** was elaborated into thionocarbonates **77a** and **77b** by the route summarized in Scheme 7. The intermediate diols **70a** and **70b** were separated and individually converted into the corresponding thionocarbonates. Our stereochemical assignments to the diols were made on the basis of proton NMR coupling constants in the hydroxy ketones **72a** and **72b**. The synthetic route for **77a** is shown in detail in Scheme 7; the same route was used to make **77b**. Unfortunately, reduction of **77a** or **77b** with Ph_3SnH or Bu_3SnH gave quite complex mixtures under what we judged to be appropriate and standard conditions for radical cyclization, and products of the desired type did not appear to be present—at least as judged by 200 MHz ^1H NMR spectra of the reaction mixtures. It would have been not only helpful to us, but also interesting, to have obtained readily isolable products, because some work has been reported[31] on stannane reduction of unsymmetrical thionocarbonates, and formation of either the less substituted or the more substituted radical—as we had wanted (*cf.* Scheme 8)—has been observed. However, exactly what controls the regiochemistry is not fully understood, and the status (primary, secondary, or tertiary) of the poten-

(25) *Cf.* Martin, S. F.; Dodge, J. A. *Tetrahedron Lett.* **1991**, *32*, 3017. We did not try the methods reported in: Tsunoda, T.; Yamamiya, Y.; Kawamura, Y.; Itô, S. *Tetrahedron Lett.* **1995**, *36*, 2529.

(26) Saïah, M.; Bessodes, M.; Antonakis, K. *Tetrahedron Lett.* **1992**, *33*, 4317.

(27) (a) Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525. (b) Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1986**, *27*, 4529. (c) Denis, R. C.; Rancourt, J.; Ghiro, É.; Boutonnet, F.; Gravel, D. *Tetrahedron Lett.* **1993**, *34*, 2091.

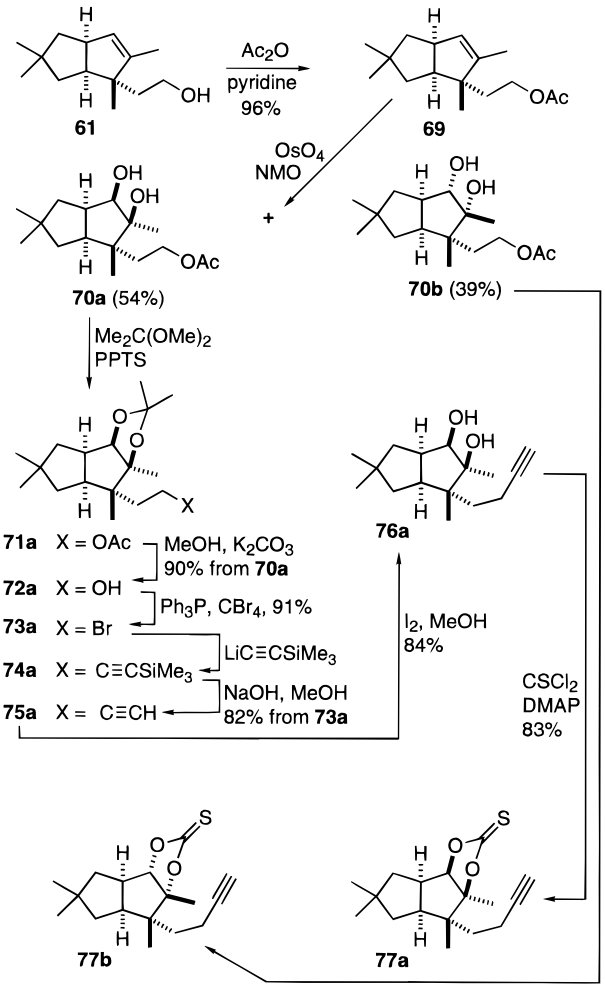
(28) (a) *Cf.* Berkowitz, W. F.; Wilson, P. J. *J. Org. Chem.* **1991**, *56*, 3097. (b) *Cf.* Kataoka, T.; Yoshimatsu, M.; Noda, Y.; Sato, T.; Shimizu, H.; Hori, M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 121.

(29) Crich, D.; Yao, Q. *J. Org. Chem.* **1995**, *60*, 84.

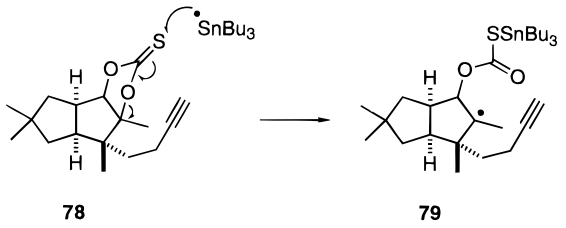
(30) E.g. (a) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. (b) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3720. (c) *Cf.* Broka, C. A.; Reichert, D. E. C. *Tetrahedron Lett.* **1987**, *28*, 1503.

(31) E.g. (a) Barton, D. H. R.; Subramanian, R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1718. (b) Redlich, H.; Sudau, W.; Paulsen, H. *Tetrahedron* **1985**, *41*, 4253. (c) Ziegler, F. E.; Zheng, Z. *J. Org. Chem.* **1990**, *55*, 1416 and references cited therein.

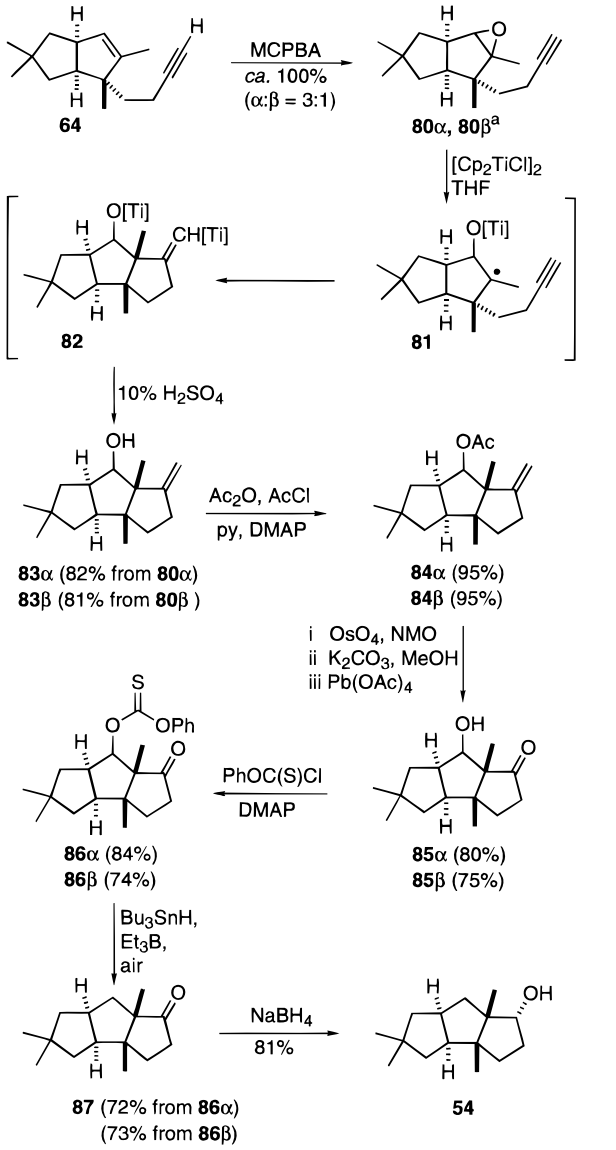
Scheme 7



Scheme 8



Scheme 9[a]



[a] Compound **80**α has oxygen anti to acetylenic chain; **80**β has the oxygen syn to the acetylenic chain.

tial carbon radical product is evidently not the only important factor.

Fortunately, radical cyclization was soon easily accomplished, after we recognized that an epoxide can be made to behave (Scheme 9) in a manner appropriate for the task in hand.

Epoxidation of enyne **64** with *m*-CPBA gave two separable epoxides, **80**α (oxygen *anti* to the acetylenic chain, 75%) and **80**β (oxygen *syn* to the acetylenic chain, *ca.* 25%).[32] Each compound was treated with bis(cyclopentadienyl)titanium(III) chloride[20] to afford the products of radical cyclization **83**α (82%) and **83**β (81%), respectively, as anticipated on the basis of the mechanism shown. From this point, a little experimentation was required to find the best way of performing the last few manipulations. Radical deoxygenation of **83**α or **83**β by means of the corresponding phenoxythiocarbonyl esters[33] gave the rearranged olefin **66**, but rearrangement could be avoided in the following way: Alcohols **83**α and **83**β were individually acetylated, giving **84**α (95%) and **84**β in (95%), dihydroxylated with OsO_4, and hydrolyzed (MeOH, K_2CO_3). The resulting triols (not shown in Scheme 9) responded in the normal way to the action of $Pb(OAc)_4$, affording hydroxy ketones **85**α and **85**β in 80% and 75% yield, respectively, from the initial acetates. Each alcohol was then deoxygenated by conversion into its phenoxythiocarbonyl ester (**85**α → **86**α, 84%; **85**β → **86**β, 74%), followed by treatment with Bu_3SnH in the presence of Et_3B and air[7] (**86**α → **87**, 72%; **86**β → **87**, 73%). When deoxygenation was attempted using initiation by AIBN in refluxing toluene, appreciable ring expansion occurred,[34] but the milder borane-mediated procedure was satisfactory. Finally, reduction with $NaBH_4$ (81%) gave crystalline (±)-ceratopicanol.

(32) In the preliminary communication (ref 1b) footnote *a* of Scheme 2 should refer to the *anti* isomer, and footnote *b* should refer to the *syn* isomer. Stereochemical assignments to the epoxides were made by NOE measurements on the derived ketone **85**β (see the Experimental Section for **85**β).

(33) Robins, M. J.; Wilson, J. S.; Hansske, F. *J. Am. Chem. Soc.* **1983**, *105*, 4059.

(34) *Cf.* Dowd, P.; Zhang, W. *Chem. Rev.* **1993**, *93*, 2091.

Experimental Section

Argon was purified by passage through a column (3.5 × 42 cm) of BASF R-311 catalyst and then through a similar column of Drierite. Glassware was dried in an oven for at least 3 h before use (120 °C) and either cooled in a desiccator over Drierite or assembled quickly, sealed with rubber septa, and allowed to cool under a slight static pressure of argon. Reaction mixtures were stirred by Teflon-coated magnetic stirring bars.

Solvents for chromatography or extractions were distilled before use. Petroleum ether refers to the fraction bp 35−60 °C.

Products were isolated from solution by evaporation under water pump vacuum at, or below, 30 °C, using a rotary evaporator.

Temperatures recorded for Kugelrohr distillations refer to air-bath temperatures and are not true boiling points. The values indicate the temperature at which the distillate begins to condense in the receiving bulb.

Melting points were determined on a Kofler block melting point apparatus.

Commercial thin layer chromatography (TLC) plates (silica gel, Merck 60F-254) were used. Spots were detected by examination under UV light or by spraying the plate with a solution of phosphomolybdic acid,[35] followed by charring on a hot plate. Silica gel for flash chromatography was Merck type 60 (230−400 mesh).

Dry solvents were prepared under an inert atmosphere and transferred by oven-dried syringes. Dry THF was distilled from Na and benzophenone ketyl. Dry PhH was distilled from Na. Dry *i*-Pr_2NH, CH_2Cl_2, MeOH, pyridine, DMF, and HMPA were distilled from CaH_2, the last two solvents being distilled under water pump vacuum. Commercial (Aldrich) solutions of *n*-BuLi (in hexanes) were assumed to have the stated molarity.

The symbols s′, d′, t′, and q′ used for ^{13}C NMR spectra indicate 0, 1, 2,or 3 attached protons.

***cis*-(±)-4-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2-cyclopenten-1-ol (20).** NaH (804.0 mg, 60% w/w in oil, 20.10 mmol) was washed with hexane (2 × 5 mL) and suspended in THF (30 mL). A solution of diol **19**[36] (2.012 g, 20.10 mmol) in THF (10 mL plus 2 mL as a rinse) was added dropwise to the stirred suspension, and vigorous stirring was continued for 1 h. *t*-$BuMe_2SiCl$ (3.0283 g, 20.10 mmol) in THF (5 mL plus 2 mL as a rinse) was added, and stirring was continued overnight. The mixture was poured into a solution of Et_2O (200 mL) and MeOH (50 mL), and the suspension was filtered through a pad (5 × 3 cm) of flash chromatography silica gel. The pad was washed with EtOAc (300 mL), and the filtrate was evaporated. Flash chromatography of the residue over silica gel (5 × 15 cm), using first 20% EtOAc−hexane and then 1:1:3 MeOH−EtOAc−hexane, gave unreacted diol **19** (205 mg, 10%) and alcohol **20** (3.705 g, 86%; 96% after correction for recovered starting material) as a pure (TLC, silica, 20% EtOAc−hexane), colorless oil: FTIR (CH_2Cl_2 cast) 3340 cm^{-1}; ^1H NMR ($CDCl_3$ 200 MHz) δ 0.07 (s, 6 H), 0.88 (s, 9 H), 1.48 (ddd, J = 14.0, 4.5, 4.5 Hz, 1 H), 2.19 (br s, 1 H), 2.66 (ddd, 14.0, 7.0, 7.0 Hz, 1 H), 4.51−4.67 (m, 2 H), 5.82−5.93 (m, 2 H); ^{13}C NMR ($CDCl_3$ 50.3 MHz) (two signals overlap) δ −4.62, 18.17, 25.92, 44.74, 75.18, 135.64, 136.97; exact mass m/z calcd for $C_7H_{13}O_2Si$ (M − *t*-Bu) 157.0685, found 157.0682. An analytical sample was prepared by Kugelrohr distillation (65 °C, 0.075 mmHg). Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34. Found: C, 61.43; H, 10.42.

***trans*-(±)-4-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2-cyclopenten-1-yl Benzoate (21).** Ph_3P (1.272 g, 4.85 mmol) and benzoic acid (592.4 mg, 4.85 mmol) were added successively to a stirred solution of alcohol **20** (520 mg, 2.43 mmol) in THF (20 mL) at room temperature. Diethyl azodicarboxylate (0.76 mL, 4.85 mmol) in THF (4 mL) was then added dropwise (*ca.* 5 min), and stirring was continued for 4 h. The solvent was evaporated, and flash chromatography of the residue over silica gel (4 × 15 cm), using 5% EtOAc−hexane, gave benzoate **21** (748.1 mg, 97%) as a pure (TLC, silica, 5% EtOAc−hexane), colorless oil: FTIR (CH_2Cl_2 cast) 1719 cm^{-1}; ^1H NMR ($CDCl_3$ 200 MHz) δ 0.10 (s, 6 H), 0.92 (s, 9 H), 2.10−2.38 (m, 2 H), 5.07−5.16 (m, 1 H), 5.98−6.11 [m, 3 H (contains singlet at δ 6.08)], 7.35−7.58 (m, 3 H), 7.96−8.06 (m, 2 H); ^{13}C NMR ($CDCl_3$ 50.3 MHz) δ −4.66, 18.19, 25.87, 41.16, 76.33, 76.41, 128.27, 129.55, 130.40, 131.46, 132.85, 141.05, 166.49; exact mass m/z calcd for $C_{18}H_{26}O_3Si$ 318.1651, found 318.1650. Anal. Calcd for $C_{18}H_{26}O_3Si$: C, 67.88; H, 8.23. Found: C, 68.13; H, 8.39.

***trans*-(±)-4-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2-cyclopenten-1-ol (22).** A solution of ester **21** (2.326 g, 7.30 mmol) in THF (10 mL) was added dropwise at room temperature to a stirred suspension of $LiAlH_4$ (554.4 mg, 14.61 mmol) in THF (31 mL). Stirring was continued for 15 min, and then the mixture was quenched by successive addition of water (0.6 mL), 15% aqueous NaOH (0.6 mL), and water (1.8 mL). The resulting mixture was stirred at room temperature for 20 min and filtered through a pad (5 × 3 cm) of Celite. The pad was washed with EtOAc, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (5 × 15 cm), using first CH_2Cl_2 and then 10% EtOAc−CH_2Cl_2, gave alcohol **22** (1.4755 g, 94%) as a pure (^1H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3333 cm^{-1}; ^1H NMR ($CDCl_3$ 200 MHz) δ 0.05 (s, 6 H), 0.87 (s, 9 H), 1.80 (br s, 1 H), 1.97−2.04 (m, 2 H), 4.94−5.10 (m, 2 H), 5.88−5.95 (m, 2 H); ^{13}C NMR ($CDCl_3$ 50.3 MHz) δ −4.62, 18.22, 25.92, 44.54, 76.24, 76.41, 135.55, 136.36; exact mass m/z calcd for $C_{11}H_{22}O_2Si$ 214.1389, found 214.1388. An analytical sample was prepared by Kugelrohr distillation (111 °C, 15 mmHg). Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34. Found: C, 61.61; H, 10.41.

***trans*-(±)-(1,1-Dimethylethyl)[[4-(ethenyloxy)-2-cyclopenten-1-yl]oxy]dimethylsilane (23).** $Hg(OAc)_2$ (462.7 mg, 6.42 mmol) was added at room temperature to a solution of alcohol **22** (1.3755 g, 6.42 mmol) in freshly distilled ethyl vinyl ether (70 mL), and the resulting solution was refluxed for 18 h. Anhydrous K_2CO_3 (4.0 g) was added to the cooled mixture, and the excess of ethyl vinyl ether was evaporated (water pump). The residue was taken up in CH_2Cl_2 (50 mL) and filtered through a pad (3 × 5 cm) of flash chromatography silica gel, using first CH_2Cl_2 and then EtOAc. The CH_2Cl_2 filtrate was evaporated to give vinyl ether **23** (1.234 g, 80%, 99% after correction for recovered starting material) as a colorless oil containing trace impurities (^1H NMR, 200 MHz): FTIR (CH_2Cl_2 cast) 2955, 2930, 2857, 1640, 1611, 1370, 1254, 1192, 1178, 1124, 1072, 1040, 978, 904, 857, 836, 814, 775 cm^{-1}; ^1H NMR ($CDCl_3$ 200 MHz) δ 0.08 (s, 6 H), 0.88 (s, 9 H), 1.96 (ddd, J = 14.5, 7.0, 4.0 Hz, 1 H), 2.20 (ddd, J = 14.5, 7.0, 2.5 Hz, 1 H), 4.01 (dd, J = 6.5, 2.0 Hz, 1 H), 4.21 (dd, J = 14.0, 2.0 Hz, 1 H), 4.99−5.12 (m, 2 H), 5.95−6.04 (m, 2 H), 6.35 (dd, J = 14, 6.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$ 50.3 MHz) δ −4.64, 18.19, 25.91, 41.01, 76.45, 82.34, 88.16, 131.67, 140.22, 150.57; exact mass m/z calcd for $C_{13}H_{24}O_2Si$ 240.1545, found 240.1549. A satisfactory combustion analysis could not be obtained.

Evaporation of the EtOAc filtrate gave the starting alcohol **22** (263.3 mg, 19%).

***trans*-(±)-5-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2-cyclopentene-1-acetaldehyde (24).** A solution of vinyl ether **23** (1.153 g, 4.80 mmol) in decalin (30 mL) was refluxed (bath temperature 200 °C) for 20 min. The mixture was cooled, diluted with hexane (50 mL), and filtered through a pad (5 × 3 cm) of flash chromatography silica gel. The pad was washed with hexane (100 mL), and the filtrate was discarded. The pad was then washed with EtOAc (200 mL), and the filtrate was evaporated. Flash chromatography of the residue over silica gel (4 × 14 cm), using 5% EtOAc−hexane, gave aldehyde **24** (1.042 g, 90%) as a pure (^1H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 1727 cm^{-1}; ^1H NMR ($CDCl_3$ 200 MHz) δ 0.04 (s, 6 H), 0.87 (s, 9 H), 2.16−2.64 (m, 4 H), 2.92−3.06 (m, 1 H), 4.05 (ddd, J = 7.0, 5.0, 5.0 Hz, 1 H), 5.56−5.71 (m, 2 H), 9.77 (t, J = 2.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$ 50.3 MHz) δ −4.77, −4.46, 18.00, 25.84, 41.38, 47.26, 48.83, 78.53, 129.19, 131.38, 201.64; exact mass m/z calcd for $C_9H_{15}O_2Si$ (M − *t*-Bu)

(35) Phosphomolybdic acid (15 g) and ceric ammonium sulfate (2.5 g) dissolved in a mixture of water (985 mL) and concentrated sulfuric acid (15 mL).

(36) Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876.

183.0841, found 183.0839. An analytical sample was prepared by Kugelrohr distillation (55 °C, 0.005 mmHg). Anal. Calcd for $C_{13}H_{24}O_2Si$: C, 64.95; H, 10.06. Found: C, 65.07; H, 9.86.

***trans*-(±)-5-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2-cyclopentene-1-ethanol (25).** A solution of aldehyde **24** (299.5 mg, 1.25 mmol) in THF (4 mL plus 1 mL as a rinse) was added at room temperature to a stirred suspension of $LiAlH_4$ (95 mg, 2.49 mmol) in THF (5 mL). The mixture was stirred for 15 min and then quenched by successive addition of water (0.1 mL), 15% aqueous NaOH (0.1 mL), and water (0.3 mL). Stirring was continued for 30 min, and the mixture was then filtered through a pad (3 × 2 cm) of Celite. The pad was washed with EtOAc, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (2 × 14 cm), using 15% EtOAc−hexane, gave alcohol **25** (269.2 mg, 89%) as a pure (TLC, silica, 15% EtOAc−hexane), colorless oil: FTIR (CH_2Cl_2 cast) 3346 cm^{-1}; ^1H NMR ($CDCl_3$ 200 MHz) δ 0.08 (s, 6 H), 0.88 (s, 9 H), 1.50−1.77 (m, 2 H), 2.06 (br s, 1 H), 2.15−2.30 (m, 1 H), 2.49−2.70 (m, 2 H), 3.6−3.79 (m, 2 H), 4.04−4.16 (m, 1 H), 5.53−5.64 (m, 2 H); ^{13}C NMR ($CDCl_3$ 50.3 MHz) δ −4.71, −4.16, 18.04, 25.88, 36.31, 41.60, 51.19, 61.51, 79.52, 127.90, 132.89; exact mass *m*/*z* calcd for $C_9H_{17}O_2Si$ (M − *t*-Bu) 185.0998, found 185.0996. An analytical sample was prepared by Kugelrohr distillation (120 °C, 14 mmHg). Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.74; H, 10.63.

***trans*-(±)-[[2-(2-Bromoethyl)-3-cyclopenten-1-yl]oxy]-(1,1-dimethylethyl)dimethylsilane (26).** Ph_3P (582.5 mg, 2.22 mmol) and CBr_4 (736.5 mg, 2.22 mmol) were added successively to a cooled (0 °C) and stirred solution of alcohol **25** (269.2 mg, 1.11 mmol) in dry CH_2Cl_2 (15 mL). The cooling bath was removed, and after 30 min, the mixture was filtered through a pad (3 × 2 cm) of flash chromatography silica gel, using CH_2Cl_2. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 × 14 cm), using first hexane and then 5% EtOAc−hexane, gave bromide **26** (326.4 mg, 96%) as a pure (^1H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2955, 2929, 2895, 2857, 1472, 1256, 1110, 1086, 904, 875, 837, 775, 709 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.84 (s, 9 H), 1.72−2.09 (m, 2 H), 2.15−2.29 (m, 1 H), 2.50−2.74 (m, 2 H), 3.42 (td, J = 7.5, 1.0 Hz, 2 H), 4.06 (dt, J = 7.0, 4.5 Hz, 1 H), 5.56−5.70 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.64, −4.32, 18.07, 25.91, 31.39, 36.97, 41.69, 53.43, 78.60, 128.69, 131.38; exact mass *m*/*z* calcd for $C_9H_{16}OBrSi$ (M − *t*-Bu) 247.0154, found 247.0148. An analytical sample was prepared by Kugelrohr distillation (110 °C, 15 mmHg). Anal. Calcd for $C_{13}H_{25}OBrSi$: C, 51.14; H, 8.25. Found: C, 51.27; H, 8.36.

***trans*-(±)-(1,1-Dimethylethyl)dimethyl[[2-(3-butynyl)-3-cyclopenten-1-yl]oxy]silane (27).** Acetylene [purified by passage through a cold trap (−78 °C), a bubbler containing concentrated H_2SO_4, a tube (15 × 2 cm) packed with NaOH pellets, and then a tube (26 × 1.5 cm) packed with Drierite] was bubbled through cold (−78 °C) THF (10 mL) for 12 min. *n*-BuLi (1.6 M in hexanes, 1.1 mL, 1.75 mmol) was added dropwise, and the resulting mixture was stirred for 10 min. Bromide **26** (178.3 mg, 0.58 mmol) in THF (2 mL plus 1 mL as a rinse) was then added, followed by HMPA (1.0 mL). The cooling bath was removed, and stirring was continued for 3 h. The mixture was then quenched with saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (3 × 20 mL). The combined extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 15 cm), using 10% CH_2Cl_2−hexane, gave enyne **27** (130.5 mg, 89%) as a pure (^1H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3313, 2955, 2929, 2889, 2857, 1472, 1463, 1361, 1256, 1111, 1093, 1071, 1006, 905, 875, 836, 815, 775, 710, 631 cm^{-1}; ^1H NMR ($CDCl_3$ 200 MHz) δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 1.39−1.76 (m, 2 H), 1.93 (t, J = 2.6 Hz, 1 H), 2.14−2.27 (m, 3 H), 2.45−2.75 (m, 2 H), 4.05 (dt, J = 6.7, 4.4 Hz, 1 H), 5.64 (s, 2 H); ^{13}C NMR ($CDCl_3$ 50.3 MHz) δ −4.63, −4.35, 16.84, 18.11, 25.94, 32.32, 42.00, 53.80, 68.33, 78.50, 84.49, 128.41, 132.10; exact mass *m*/*z* calcd for $C_{11}H_{17}OSi$ (M − *t*-Bu) 193.1049, found 193.1039. An analytical sample was prepared by Kugelrohr distillation (105 °C, 14 mmHg). Anal. Calcd for $C_{15}H_{26}OSi$: C, 71.93; H, 10.46. Found: C, 72.16; H, 10.60.

(1α,3aα,6aα)-(±)-(1,1-Dimethylethyl)dimethyl[octahydro-4-methylene-1-pentalenyl)oxy]silane (29). Et_3B (1.0 M in hexane, 0.80 mL, 0.80 mmol) was added dropwise to a stirred solution of enyne **27** (201.4 mg, 0.80 mmol) and Bu_3SnH (0.27 mL, 1.00 mmol) in hexane (55 mL). The mixture was stirred at room temperature for an arbitrary period of 3 h (protection from atmospheric moisture by a Drierite tube). Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 14 cm), using first hexane followed by 10% CH_2Cl_2−hexane, gave olefin **29** (154.2 mg, 76%; 85% after correction for recovered starting material) as a pure (^1H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2954, 2936, 2930, 2894, 2857, 1472, 1462, 1361, 1255, 1179, 1122, 1092, 1063, 1025, 1006, 880, 866, 835, 774 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.02 (s, 3 H), 0.03 (s, 3 H), 0.87 (s, 9 H), 1.13−1.91 (m, 5 H), 1.98−2.45 (m, 4 H), 2.86−3.02 (m, 1 H), 3.86 (dd, J = 3.5, 3.5 Hz, 1 H), 4.73 (dddd, J = 2.0, 2.0, 2.0, 2.0 Hz, 1 H), 4.81 (dddd, J = 2.0, 2.0, 2.0, 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.64, −4.54, 18.17, 25.94, 29.33, 30.79, 34.27, 34.94, 46.29, 53.43, 80.00, 104.19, 158.47; exact mass *m*/*z* calcd for $C_{15}H_{28}OSi$ 252.1909, found 252.1905. An analytical sample was prepared by Kugelrohr distillation (126 °C, 14 mmHg). Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.51; H, 11.15.

(3aα,4α,6aα)-(±)-4-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]hexahydro-1(2*H*)-pentalenone (30). OsO_4 (2.5 w/w % in 2-methyl-2-propanol, 3.4 mL, 0.27 mmol) was added dropwise to a stirred solution of olefin **29** (687.0 mg, 2.72 mmol) in acetone (2.5 mL) and water (5.0 mL). 4-Methylmorpholine *N*-oxide monohydrate (735.3 mg, 5.44 mmol) was added in one portion, and stirring was continued for 3 h. The mixture was saturated with $MgSO_4$ and filtered through a pad (5 × 3 cm) of flash chromatography silica gel, using EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (3 × 15 cm), using 50% EtOAc−hexane, gave a mixture (787.7 mg, 99%) of two diastereomeric diols in a 12:1 ratio (^1H NMR, 200 MHz). The diastereomers were separated by flash chromatography over silica gel (3 × 25 cm), using EtOAc−hexane mixtures containing from 35 to 50% EtOAc. The minor diastereoisomer had: FTIR (CH_2Cl_2 cast) 3385 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.03 (s, 6 H), 0.86 (s, 9 H), 1.18−1.88 (m, 8 H), 2.0 (br s, 2 H), 2.2−2.4 (m, 2 H), 3.48 (s, 2 H), 3.90 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.64, −4.55, 18.12, 23.56, 25.91, 27.52, 36.01, 36.46, 47.81, 52.86, 69.53, 80.49, 82.40; exact mass *m*/*z* calcd for $C_{15}H_{30}O_3Si$ 286.1964, found 286.1966. An analytical sample was prepared by Kugelrohr distillation (164 °C, 14 mmHg). Anal. Calcd for $C_{15}H_{30}O_3Si$: C, 62.89; H, 10.56. Found: C, 63.01; H, 10.52.

The major diastereoisomer had: FTIR (CH_2Cl_2 cast) 3376 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.02 (s, 3 H), 0.03 (s, 3 H), 0.70−0.98 (s, 9 H), 0.99−1.19 (m, 1 H), 1.30−2.20 [m 9 H (includes br s at δ 1.95)], 2.35−2.58 (m, 2 H), 3.58 (d, J = 11 Hz, 1 H), 3.67 (d, J = 11 Hz, 1 H), 3.75−3.84 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) −4.59, 18.08, 25.54, 25.87, 27.78, 33.92, 35.65, 51.26, 52.03, 66.96, 81.15, 84.89; exact mass *m*/*z* calcd for $C_{15}H_{30}O_3Si$ 286.1964, found 286.1965. Anal. Calcd for $C_{15}H_{30}O_3Si$: C, 62.89; H, 10.56. Found: C, 62.83; H, 10.61.

K_2CO_3 (127.8 mg, 0.92 mmol) and $Pb(OAc)_4$ (273.3 mg, 0.62 mmol) were added successively to a stirred and cooled (0 °C) solution of the above diols (88.3 mg, 0.31 mmol) in CH_2Cl_2 (10 mL). After 10 min the cold bath was removed and stirring was continued for 50 min. The mixture was then filtered through a pad (3 × 2 cm) of flash chromatography silica gel, using EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 × 15 cm), using 5% EtOAc−hexane, gave ketone **30** (73.0 mg, 93%) as a pure (^1H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 1740 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.04 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 1.36−1.82 (m, 4 H), 2.0−2.40 (m, 4 H), 2.54−2.76 (m, 2 H), 3.90−4.00 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.78, −4.63, 18.04, 23.97, 25.80, 26.52, 34.51, 37.96, 49.97, 50.12, 79.44, 222.64; exact mass *m*/*z* calcd for $C_{14}H_{26}O_2Si$ 254.1702, found 254.1696. An analytical sample was prepared by Kugelrohr distillation (152 °C, 15 mmHg). Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30. Found: C, 65.90; H, 10.48.

(3aα,4α,6aα)-(±)-4-[[(1,1-Dimethylethyl)dimethylsilyl]-oxy]-4,5,6,6a-tetrahydro-1(3a*H*)-pentalenone (31).[37] A solution of ketone **30** (198.9 mg, 0.78 mmol) in THF (2 mL plus 1 mL as a rinse) was added to a stirred and cooled (−78 °C) solution of LDA [prepared by addition of *n*-BuLi (1.6 M in hexanes, 0.98 mL, 1.56 mmol) to a stirred and cooled (−78 °C) solution of *i*-Pr_2NH (0.22 mL, 1.56 mmol) in THF (10 mL)]. After 30 min the mixture was transferred by cannula to a stirred solution of diphenyl disulfide (204.3 mg, 0.94 mmol) in a mixture of THF (3 mL) and HMPA (1.0 mL). After 1.5 h the mixture was poured into a separatory funnel containing EtOAc (50 mL) and 0.5 M hydrochloric acid (10 mL). The layers were shaken and separated, and the organic phase was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated to give the crude sulfides as a yellow oil. The oil was taken up in CH_2Cl_2 (15 mL), and solid $NaHCO_3$ (120.0 mg, 1.43 mmol) was added. The mixture was cooled to −78 °C and *m*-CPBA (175.4 mg, 80−85%, 0.84 mmol) added in one portion with stirring. The cold bath was removed and the mixture allowed to attain room temperature. Additional *m*-CPBA (55 mg and then 50 mg, 0.50 mmol total) was added until all the sulfide had been oxidized (TLC control, silica, 10% EtOAc−hexane). The mixture was poured into a separatory funnel containing EtOAc (50 mL) and 10% aqueous Na_2SO_3 (10 mL). The organic layer was separated and washed with saturated aqueous $NaHCO_3$ (2 × 10 mL) and brine. The combined aqueous washes were extracted once with EtOAc. All the organic extracts were combined, dried ($MgSO_4$), and evaporated. The crude sulfoxides were taken up in PhMe (15 mL), and $(MeO)_3P$ (0.18 mL, 1.56 mmol) was added. The resulting mixture was refluxed for 5 h, cooled, and filtered through a pad (3 × 2 cm) of flash chromatography silica gel, using hexane. The filtrate was discarded, and the pad was washed with EtOAc. Evaporation of the resulting filtrate and flash chromatography of the residue over silica gel (2 × 15 cm), using 5% EtOAc−hexane, gave enone **31** (143.1 mg, 73%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.04 (s, 3 H), 0.06 (s, 3 H), 0.87 (s, 9 H), 1.24−1.46 (m,1 H), 1.48−1.63 (m, 1 H), 1.74−1.89 (m, 1 H), 2.02−2.27 (m, 1 H), 2.79 (ddd, J = 10.0, 5.5, 1.5 Hz, 1 H), 3.13−3.22 (m, 1 H), 4.10 (br d, J = 4.0 Hz, 1 H), 6.10 (dd, J = 5.5, 2.0 Hz, 1 H), 7.54 (dd, J = 5.5, 3.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.82, −4.66, 18.04, 25.79, 26.68, 32.73, 48.62, 57.62, 75.09, 135.36, 163.88, 212.95; exact mass *m*/*z* calcd for $C_{14}H_{24}O_2Si$ 252.1545, found 252.1539. An analytical sample was prepared by Kugelrohr distillation (90 °C, 0.10 mmHg). Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.90; H, 9.36.

(1α,3a*β*,4*β*,6a*β*)-(±)-4-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-1,3a,4,5,6,6a-hexahydro-1-pentalenol (32). $NaBH_4$ (214.5 mg, 5.67 mmol) was added to a stirred and cooled (water bath at room temperature) mixture of enone **31** (143.1 mg, 0.57 mmol) and $CeCl_3 \cdot 7H_2O$ (211.2 mg, 0.57 mmol) in MeOH (10 mL). After 15 min, the reaction was quenched by addition of water, and the mixture was extracted with EtOAc (3 × 25 mL). The aqueous layer was acidified with 0.5 M hydrochloric acid and extracted with EtOAc (1 × 25 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 10% EtOAc−hexane, gave allylic alcohol **32** (131.4 mg, 91%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3330 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.03 (s, 3 H), 0.05 (s, 3 H), 0.88 (s, 9 H), 1.43−1.85 (m, 5 H), 2.83−3.01 (m, 2 H), 3.98 (td, J = 4.0, 1.5 Hz, 1 H), 4.77−4.86 (m, 1 H), 5.66 (dt, J = 5.5, 2.0 Hz, 1 H), 5.78 (dt, J = 5.5, 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.71, −4.60, 18.14, 22.78, 25.90, 35.54, 43.76, 60.90, 77.84, 78.42, 134.44, 134.57; exact mass *m*/*z* calcd for $C_{10}H_{17}O_2Si$ (M − *t*-Bu) 197.0998, found 197.0993. An analytical sample was prepared by Kugelrohr distillation (80 °C, 0.06 mmHg). Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.09; H, 10.30. Found: C, 65.89; H, 10.50.

(37) Cotterill, I. C.; Finch, H.; Highcock, R. M.; Holt, R. A.; Mahon, M. F.; Molloy, K. C.; Morris, J. G.; Roberts, S. M.; Short, K. M.; Sik. V. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1353.

(1α,3a*β*,4*β*,6a*β*)-(±)-(1,1-Dimethylethyl)[[4-(ethenyloxy)-1,2,3,3a,4,6a-hexahydro-1-pentalenyl]oxy]dimethylsilane (33). NaOAc (25.3 mg, 0.31 mmol) and $Hg(OAc)_2$ (49.2 mg, 0.15 mmol) were added to a stirred solution of alcohol **32** (39.3 mg, 0.15 mmol) in freshly distilled ethyl vinyl ether (12 mL). The resulting suspension was refluxed for 48 h and then cooled to room temperature. Anhydrous K_2CO_3 was added to the mixture, and the excess of ethyl vinyl ether was evaporated. The residue was taken up in 2:3 CH_2Cl_2−hexane and filtered through a pad (2 × 3 cm) of flash chromatography silica gel. The filtrate was evaporated to give vinyl ether **33** (26.8 mg, 72%) as a colorless oil containing trace impurities (^{1}H NMR, 200 MHz): FTIR (CH_2Cl_2 cast) 2955, 2929, 2886, 2857, 1635, 1610, 1472, 1463, 1362, 1320, 1254, 1193, 1157, 1093, 1055, 1005, 987, 961, 945, 907, 863, 834, 813, 775 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.03 (s, 3 H), 0.05 (s, 3 H), 0.87 (s, 9 H), 1.35−1.80 [m, 4 H (includes t at δ 1.71, J = 5.0 Hz)], 2.89−3.13 (m, 2 H), 3.96−4.04 (m, 2 H), 4.24 (dd, J = 14.0, 2.0 Hz, 1 H), 4.87 (dd, J = 8.0, 1.5 Hz, 1 H), 5.68 (dt, J = 5.5, 2.0 Hz, 1 H), 5.82 (dt, J = 5.5, 2.0 Hz, 1 H), 6.43 (dd, J = 14.0, 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.71, −4.59, 18.12, 23.01, 25.90, 35.21, 42.79, 60,86, 78.28, 84.09, 87.58, 131.20, 135.36, 151.45; exact mass *m*/*z* calcd for $C_{14}H_{25}OSi$ (M − C_2H_3O) 237.1675, found 237.1670. A satisfactory combustion analysis could not be obtained.

(1α,3a*β*,6*β*,6a*β*)-(±)-6-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-1,3a,4,5,6,6a-hexahydro-1-pentaleneethanol (35). *i*-Bu_3Al (1.0 M in PhMe, 0.38 mL, 0.38 mmol) was added to a cooled (−78 °C) and stirred solution of vinyl ether **33** (26.8 mg, 0.096 mmol) in CH_2Cl_2 (4.0 mL). The cold bath was removed, and after 1 h, the mixture was recooled to −78 °C and quenched by addition of 0.5 M hydrochloric acid. The mixture was then poured into a separatory funnel containing 0.5 M hydrochloric acid and EtOAc. The layers were separated, and the aqueous phase was extracted with EtOAc. The combined organic fractions were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm), using 10−15% EtOAc−hexane, gave alcohol **35** (25.7 mg, 95%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3360 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 1.16−1.73 (m, 4 H), 1.79−2.05 (m, 2 H), 2.05−2.33 (m, 1 H), 2.56 (td, J = 8.5, 5.5 Hz, 1 H), 2.79−2.98 (m, 1 H), 3.11−3.28 (m, 1 H), 3.61−3.88 (m, 2 H), 4.05 (q, J = 6.0 Hz, 1 H), 5.41−5.53 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.44, −3.94, 18.04, 25.94, 27.81, 33.04, 35.36, 44.36, 48.94, 53.17, 63.02, 75.33, 132.83, 137.43; exact mass *m*/*z* calcd for $C_{12}H_{21}O_2Si$ (M − *t*-Bu) 225.1311, found 225.1314.

(1α,3aα,6*β*,6aα)-(±)-[[6-(2-Bromoethyl)-1,2,3,3a,6,6a-hexahydro-1-pentalenyl]oxy](1,1-dimethylethyl)dimethylsilane (36). Ph_3P (1.0467 g, 4.0 mmol) and CBr_4 (1.324 g, 4.0 mmol) were added successively to a cooled (0 °C) and stirred solution of alcohol **35** (563.7 mg, 2.0 mmol) in CH_2Cl_2 (25 mL). The cold bath was removed, and after 30 min, the reaction mixture was filtered through a pad (3 × 2 cm) of flash chromatography silica gel, using CH_2Cl_2. Evaporation of the filtrate and flash chromatography of the residue over silica gel (3 × 15 cm), using 5% CH_2Cl_2−hexane, gave bromide **35** (658.9 mg, 96%) as a pure (TLC, silica, 5% CH_2Cl_2−hexane), colorless oil: FTIR (CH_2Cl_2 cast) 2954, 2929, 2884, 2856, 1742, 1462, 1475, 1362, 1256, 1111, 1103, 1049, 836, 774 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 1.20−1.39 (m, 1 H), 1.47−1.65 (m, 2 H), 1.82−2.00 (m, 2 H), 2.12−2.23 (m, 1 H), 2.54 (td, J = 8.5, 5.0 Hz, 1 H), 2.91−3.00 (m, 1 H), 3.18−3.26 (m, 1 H), 3.45−3.59 (m, 2 H), 4.04 (ddd, J = 5.0, 5.0, 5.0 Hz, 1 H), 5.47 (ddd, J = 5.5, 2.0, 2.0 Hz, 1 H), 5.53 (ddd, J = 5.5, 2.6, 2.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.52, −3.90, 17.97, 25.94, 28.02, 33.03, 34.17, 35.36, 45.93, 49.10, 52.74, 75.08, 131.22, 135.25; exact mass *m*/*z* calcd for $C_{12}H_{20}OSiBr$ (M − *t*-Bu) 287.0467, found 287.0459.

(1α,3aα,6*β*,6aα)-(±)-[[6-(3-Butynyl)-1,2,3,3a,6,6a-hexahydro-1-pentalenyl]oxy](1,1-dimethylethyl)dimethylsilane (37). Acetylene [purified by passage through a cold trap (−78 °C), a bubbler containing concentrated H_2SO_4, a tube (15 × 2 cm) packed with NaOH pellets, and then a tube (26 × 1.5

cm) packed with Drierite] was bubbled through cold (−78 °C) THF (30 mL) for 20 min. *n*-BuLi (1.6 M in hexanes, 3.6 mL, 5.72 mmol) was added dropwise, and the resulting mixture was stirred for 15 min. Bromide **36** (658.9 mg, 1.91 mmol) in THF (5 mL plus 2 mL as a rinse) was then added, followed by HMPA (4 mL). The cooling bath was removed, and stirring was continued for 1 h. The mixture was quenched with water and extracted with hexane. The organic extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 15 cm), using 10% CH_2Cl_2−hexane, gave enyne **37** (517.6 mg, 93%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3313, 2953, 2930, 2892, 2885, 2856, 2105, 1472, 1462, 1361, 1256, 1103, 1068, 1053, 1026, 1006, 836, 774, 632 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.02 (s, 3 H), 0.04 (s, 3 H), 0.88 (s, 9 H), 1.23−1.40 (m, 1 H), 1.40−1.62 (m, 3 H), 1.73−2.02 [m, 3 H (includes t at δ 1.95, J = 3.0 Hz)], 2.23−2.36 (m, 2 H), 2.52 (ddd, J = 8.5, 4.5, 4.5 Hz, 1 H), 2.82−2.97 (m, 1 H), 3.14−3.29 (m, 1 H), 4.05 (ddd, J = 4.5, 4.5, 4.5 Hz, 1 H), 5.49 (br s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −4.53, −3.99, 18.00, 18.17, 25.98, 28.27, 29.91, 35.28, 46.60, 49.50, 53.11, 68.39, 75.19, 84.56, 132.19, 134.64; exact mass m/z calcd for $C_{14}H_{21}OSi$ (M − *t*-Bu) 233.1362, found 233.1363. An analytical sample was prepared by Kugelrohr distillation (118 °C, 11 mmHg). Anal. Calcd for $C_{18}H_{30}OSi$: C, 74.42; H, 10.41. Found: C, 74.56; H, 10.54.

(3α,3aα,3bα,6aα,7aα)-(±)-[(Decahydro-6-methylene-1*H*-cyclopenta[*a*]pentalen-3-yl)oxy](1,1-dimethylethyl)dimethylsilane (38). Bu_3SnH (73 μL, 0.27 mmol) and AIBN (4.2 mg, 0.026 mmol) were added to a solution of enyne **37** (58.1 mg, 0.20 mmol) in PhMe (10 mL), and the mixture was refluxed for 45 min, cooled, and evaporated. Flash chromatography of the residue over silica gel (2 × 16 cm), using 5% CH_2Cl_2−hexane, gave olefin **38** (46.4 mg, 79%) as a pure (^{1}H NMR, 400 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2949, 2936, 2898, 2858, 1471, 1462, 1254, 1110, 1068, 1048, 1036, 901, 878, 854, 835, 774 cm^{-1}; ^{1}H NMR ($CDCl_3$ 400 MHz) δ 0.02 (s, 3 H), 0.03 (s, 3 H), 0.86 (s, 9 H), 0.92−1.02 (m, 1 H), 1.23−1.32 (m, 1 H), 1.32−1.48 (m, 1 H), 1.53−1.95 (m, 5 H), 2.25−2.37 (m, 1 H), 2.38−2.49 (m, 2 H), 2.53−2.73 (m, 2 H), 2.84 (dd, J = 18.0, 9.0 Hz, 1 H), 4.05 (dd, J = 8.0, 4.0 Hz, 1 H), 4.71−4.74 (m, 1 H), 4.76−4.79 (m, 1 H); ^{13}C NMR ($CDCl_3$ 100.6 MHz) δ −4.7, −4.4, 18.15, 25.96, 27.08, 29.32, 34.60, 37.16, 39.17, 45.85, 47.06, 52.80, 55.97, 76.14, 104.42, 156.39; exact mass m/z calcd for $C_{18}H_{32}OSi$, 292.2222, found 292.2218. An analytical sample was prepared by Kugelrohr distillation (125 °C, 11 mmHg). Anal. Calcd for $C_{18}H_{32}OSi$: C, 73.90; H, 11.03. Found: C, 73.76; H, 11.18.

(±)-1,2,3,4,5,6,7,8-Octahydro-1-naphthalenol (40). $CeCl_3 \cdot 7H_2O$ (4.656 g, 12.50 mmol) was added to a stirred and cooled (0 °C) solution of enone **39**[18] (1.562 g, 10.4 mmol) in MeOH (100 mL). $NaBH_4$ (0.985 g, 26.0 mmol) was added via a side-arm addition tube over 15 min, and after 2 h, water (100 mL) was added to the resulting white slurry. (Acid must be avoided in the workup in order to prevent formation of a very nonpolar UV-active compound.) The clear aqueous solution was extracted with EtOAc until extraction was complete (TLC control, silica, 1:9 EtOAc−hexane). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 1:9 EtOAc−hexane, gave alcohol **40** (1.454 g, 92%) as a pure (^{1}H NMR, 200 MHz), white solid: mp 51−53 °C; FTIR ($CHCl_3$ cast) 3319 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20−2.05 (m, 14 H), 2.15−2.45 (m, 1 H), 3.90 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 18.2 (t′), 22.8 (t′), 23.0 (t′), 27.0 (t′), 30.3 (t′), 30.6 (t′), 32.2 (t′), 68.7 (d′), 129.9 (s′), 132.7 (s′); exact mass m/z calcd for $C_{10}H_{16}O$ 152.1201, found 152.1200. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.01; H, 10.29.

2-(1,2,3,4,5,6,7,8-Octahydronaphthalen-1-yloxy)ethyl Phenyl Sulfoxide (41). Alcohol **40** (1.670 g, 10.99 mmol) in dry THF (15 mL) was added dropwise at room temperature to a stirred suspension of NaH (80% suspension in mineral oil, 330 mg, 10.99 mmol) in dry THF (50 mL). After 30 min, a solution of phenyl vinyl sulfoxide[38] (5.02 g, 32.96 mmol) in dry THF (10 mL) was added dropwise. A trace (*ca.* 1 mg) of KH (35%w/w in mineral oil) was then added as a catalyst. After 1 h, EtOAc (50 mL) and water (50 mL) were added. The aqueous phase was extracted with EtOAc until extraction was complete (TLC control, silica, 1:1 EtOAc−hexane). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using 1:1 EtOAc−hexane, gave a mixture of sulfoxide **41** and phenyl vinyl sulfoxide. This mixture was not further purified, but was used directly in the next step.

(±)-1,3,4,5,6,7-Hexahydro-4a(2*H*)-naphthaleneacetaldehyde (42). $NaHCO_3$ (35.63 g, 424 mmol) was added in one lot to a stirred solution of sulfoxide **41** (mass unrecorded, contaminated with phenyl vinyl sulfoxide) in dry, purified decalin (50 mL). The suspension was heated at 180 °C for 5 days and then cooled to room temperature. EtOAc (100 mL) and water (50 mL) were added, and the organic phase was washed with brine, dried ($MgSO_4$), and evaporated. Decalin was removed by flash chromatography, using hexane, and the desired compound was then eluted with EtOAc. Evaporation of the EtOAc eluant, and flash chromatography of the residue over silica gel (3 × 18 cm), using 15:85 CH_2Cl_2−hexane, gave aldehyde **42** (1.182 g, 60% over two steps) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (neat) 1719 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.10−2.35 (m, 14 H), 2.35−2.55 (dd, J = 14, 3 Hz, 1 H), 2.55−2.80 (dd, J = 14, 3 Hz, 1 H), 5.40−5.60 (m, 1 H), 9.75−9.90 (dd, J = 4.0, 2.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 18.7 (t′), 21.9 (t′), 25.3 (t′), 28.0 (t′), 32.2 (t′), 36.9 (t′), 37.6 (s′), 39.2 (t′), 48.3 (t′), 121.8 (d′), 140.8 (s′), 203.6 (d′); exact mass m/z calcd for $C_{12}H_{18}O$ 178.1358, found 178.1361. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.54; H, 10.14.

(±)-1,3,4,5,6,7-Hexahydro-4a(2*H*)-naphthaleneethanol (43). Aldehyde **42** (1.00 g, 5.62 mmol) in THF (10 mL) was added to a stirred and cooled (−78 °C) suspension of $LiAlH_4$ (107 mg, 2.81 mmol) in dry THF (30 mL). The mixture was allowed to warm to room temperature and then cooled to 0 °C. Water (10 mL) was added, and the aqueous solution was extracted with EtOAc until extraction was complete (TLC control, silica, 1:4 EtOAc−hexane). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 18 cm), using 1:4 EtOAc−hexane, gave alcohol **43** (933 mg, 92%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR ($CHCl_3$ cast) 3316 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.05−1.35 (m, 3 H), 1.35−1.45 (s, 1 H), 1.45−1.82 (m, 8 H), 1.82−2.05 (m, 4 H), 2.05−2.40 (m, 1 H), 3.50−3.80 (dd, J = 8.4, 7.6 Hz, 2 H), 5.30−5.50 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 19.3 (t′), 22.1 (t′), 25.6 (t′), 28.4 (t′), 32.6 (t′), 36.1 (t′), 36.8 (s′), 37.6 (t′), 39.1 (t′), 59.5 (t′), 120.7 (d′), 143.3 (s′); exact mass m/z calcd for $C_{12}H_{20}O$ 180.1514, found 180.1517. A satisfactory combustion analysis could not be obtained.

(±)-4a-(2-Bromoethyl)-1,2,3,4,4a,5,6,7-octahydronaphthalene (44). CBr_4 (1.398 g, 4.22 mmol) and Ph_3P (1.106 g, 4.22 mmol) were added successively to a stirred and cooled (0 °C) solution of alcohol **43** (744 mg, 4.13 mmol) in dry CH_2Cl_2 (20 mL). The cold bath was removed, and stirring was continued for 2.5 h. The clear solution was then filtered through a short pad (4 × 3 cm) of flash chromatography silica gel, using hexane to wash the residue completely out of the silica. The organic solution was washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3 × 20 cm), using hexane, gave bromide **44** (928 mg, 92%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2926, 2854, 1456, 1445, 1215, 807, 630 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.05−1.40 (m, 3 H), 1.40−1.85 (m, 7 H), 1.85−2.35 (m, 6 H), 3.15−3.50 (m, 2 H), 5.30−5.50 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 19.2 (t′), 22.0 (t′), 25.4 (t′), 28.2 (t′), 28.9 (t′), 32.3 (t′), 35.4 (t′), 38.3 (t′), 38.9 (t′), 39.0 (s′), 121.3 (d′), 141.7 (s′); exact mass m/z calcd for $C_{12}H_{19}{}^{79}Br$ 242.0671, found 242.0670. Anal. Calcd for $C_{12}H_{19}Br$: C, 59.27; H, 7.88. Found: C, 59.17; H, 8.09.

(38) Paquette, L. A.; Carr, R. V. C. *Organic Syntheses;* Wiley: New York, 1990; Collect. Vol. VII, p 453.

(±)-4a-(3-Butynyl)-1,2,3,4,4a,5,6,7-octahydronaphthalene (45). *n*-BuLi (1.6 M in hexanes, 5.15 mL, 8.23 mmol) was added over 5 min to a stirred and cooled (-78 °C) solution of trimethylsilyl acetylene (2.021 g, 20.58 mmol) in dry THF (20 mL). After 15 min, bromide **44** (500 mg, 2.06 mmol) in dry THF (5 mL) was added dropwise. HMPA (2 mL) was added, the cold bath was removed, and stirring was continued for 8 h. NaOMe (2.0 M in MeOH, 20 mL, 40 mmol) was then added with stirring, and after 2 h, the mixture was poured into 1:1 hexane−water (50 mL). The aqueous layer was extracted with hexane until extraction was complete (TLC control, silica, hexane). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 22 cm), using hexane, gave acetylene **45** (302 mg, 78%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR ($CHCl_3$ cast) 3310, 2118 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.00−1.40 (m, 3 H), 1.40−2.30 (m, 16 H), 5.30−5.50 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.1 (t′), 19.2 (t′), 22.0 (t′), 25.7 (t′), 28.3 (t′), 32.5 (t′), 33.9 (t′), 35.1 (t′), 37.5 (s′), 37.9 (t′), 67.7 (d′), 85.4 (s′), 121.0 (d′), 142.7 (s′); exact mass *m*/*z* calcd for $C_{14}H_{20}$ 188.1565, found 188.1565. Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.41; H, 10.99.

(±)-4a-(3-Butynyl)octahydro-3*H*-naphth[1,8a-*b*]oxirene (48). Dimethyldioxirane (0.1 M in acetone, 4.88 mL, 0.488 mmol) was added to a stirred and cooled (0 °C) solution of olefinic acetylene **45** (91.7 mg, 0.488 mmol) in bench acetone (15 mL). The cold bath was removed, and after 2 h, additional dimethyldioxirane was added at room temperature as needed (TLC control, silica, 1:19 EtOAc−hexane) in order to complete the reaction. Water (10 mL) was added, and the mixture was extracted with EtOAc until extraction was complete (TLC control, silica, 1:19 EtOAc−hexane). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 17 cm), using 1:19 EtOAc−hexane, gave a 2:1 mixture (^{1}H NMR) of diastereomeric epoxides **48** (84.0 mg, 84%) as a pure (^{1}H NMR, 200 MHz), white solid: FTIR ($CHCl_3$ cast) 3307 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.85−2.40 (m, 38 H), 2.75−3.00 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) (two signals overlap with two other signals) δ 12.5 (t′), 12.6 (t′), 15.1 (t′), 16.0 (t′), 21.0 (t′), 22.0 (t′), 23.5 (t′), 24.0 (t′), 25.8 (t′), 27.8 (t′), 29.4 (t′), 29.8 (t′), 30.4 (t′), 31.8 (t′), 32.4 (t′), 32.8 (t′), 34.4 (t′), 35.9 (t′), 59.7 (d′), 60.0 (d′), 63.8 (s′), 65.2 (s′), 67.7 (d′), 68.1 (d′), 84.9 (s′), 85.4 (s′); exact mass *m*/*z* calcd for $C_{14}H_{20}O$ 204.1514, found 204.1497. Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.07; H, 9.92.

(1*R,2*S**,6*S**)- and (1*R**,2*R**,6*S**)-(±)-11-Methylenetricyclo[4.4.3.0^{1,6}]tridecan-2-ol (51) and (52).** $TiCp_2Cl$ (628 mg, 1.49 mmol) in THF (30 mL) was added to a solution of epoxides **48** (238 mg, 2:1 mixture of diastereomers, 1.17 mmol) in dry THF (20 mL). After 14 h, aqueous 10% v/v H_2SO_4 (50 mL) was added, and the aqueous mixture was extracted with EtOAc until extraction was complete (TLC control, silica, 5% EtOAc−hexane). The combined organic extracts were washed successively with saturated aqueous $NaHCO_3$ and water and then dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.5 × 16 cm), using 5% EtOAc−hexane, gave alcohol **52** (114 mg, 48%) and alcohol **51** (67 mg, 28%) as pure (^{1}H NMR, 200 MHz), colorless solids. Alcohol **52**: mp 90−95 °C; FTIR (CH_2Cl_2 cast) 3464 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.95−2.20 (m, 17 H), 2.25−2.70 (m, 2 H), 3.30−3.60 (s, 1 H), 4.95 (t, J = 3.0 Hz, 1 H), 5.06 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 17.1 (t′), 21.6 (t′), 22.2 (t′), 29.1 (t′), 29.3 (t′), 30.2 (t′), 30.7 (t′), 33.1 (t′), 35.3 (t′), 43.5 (s′), 51.6 (s′), 75.1 (d′), 106.3 (t′), 157.7 (s′); exact mass *m*/*z* calcd for $C_{14}H_{22}O$ 206.1671, found 206.1670. A satisfactory combustion analysis could not be obtained.

Alcohol **51**: mp 97−99 °C; FTIR (CH_2Cl_2 cast) 3463 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.70−2.45 (m, 17 H), 2.45−2.65 (m, 2 H), 3.25−3.50 (two broad signals, 1 H), 4.75−4.90 (t, J = 2.0 Hz, 1 H), 4.95−5.10 (t, J = 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 19.9 (t′), 20.3 (t′), 21.6 (t′), 21.8 (t′), 27.4 (t′), 27.6 (t′), 28.1 (t′), 31.3 (t′), 36.0 (t′), 44.6 (s′), 53.3 (s′), 70.7 (d′), 105.9 (t′), 156.0 (s′); exact mass *m*/*z* calcd for $C_{14}H_{22}O$ 206.1671, found 206.1670. A satisfactory combustion analysis could not be obtained.

The more polar alcohol (**51**) showed no NOE between the methinyl hydrogen and either vinyl hydrogen, whereas the less polar isomer (**52**) showed a small (1%) NOE. On the assumption of a chair conformation for the six-membered rings, compound **51** would be expected to have the hydroxyl-bearing carbon at lower field[39] in the ^{13}C NMR spectrum than **52**. The ^{1}H NMR signal for the methinyl hydrogen of **51** should be a multiplet with one large (axial−axial) coupling; the corresponding signal for **52** should contain only small couplings. The NMR spectra show that these expectations are met and, on this basis, the stereochemistry is tentatively assigned.

(1*R,6*S**)-(±)-11-Methylenetricyclo[4.4.3.0^{1,6}]tridecan-2-one (53).** A mixture of diastereomeric alcohols **51** and **52** (53.0 mg, 0.257 mmol) in dry CH_2Cl_2 (8 mL) was added at room temperature to a stirred mixture of PCC (277 mg, 1.29 mmol) and molecular sieves (4 Å, 92 mg) in dry CH_2Cl_2 (10 mL). After 2.5 h, the brown mixture was filtered through a pad (2 × 3 cm) of flash chromatography silica gel, CH_2Cl_2 being used to wash the product completely out of the silica. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.5 × 17 cm), using 1:19 EtOAc−hexane, gave ketone **53** (46.0 mg, 88%) as a pure (^{1}H NMR, 200 MHz), colorless solid: mp 79−82 °C; FTIR ($CHCl_3$ cast) 1702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90−1.65 (m, 9 H), 1.65−2.30 (m, 6 H), 2.35−2.80 (m, 3 H), 4.40−4.65 (t, J = 4.0 Hz, 1 H), 4.65−4.95 (t, J = 4.0 Hz, 1 H); ^{13}C NMR (50.3 MHz) δ 21.5 (t′), 21.8 (t′), 23.2 (t′), 28.4 (t′), 30.1 (t′), 30.9 (t′), 32.7 (t′), 34.0 (t′), 38.3 (t′), 49.8 (s′), 63.5 (s′), 106.7 (t′), 156.9 (s′), 212.3 (s′); exact mass *m*/*z* calcd for $C_{14}H_{20}O$ 204.1514, found 204.1507. A satisfactory combustion analysis could not be obtained.

(1α,3a*β*,6a*β*)-(±)-1,3a,4,5,6,6a-Hexahydro-2,3,5,5-tetramethyl-1-pentalenol (57). DIBAL (1 M in CH_2Cl_2, 4.3 mL, 4.3 mmol) was added dropwise over *ca*. 20 min to a cooled (0 °C) and stirred solution of enone **56** (385.1 mg, 2.16 mmol) in CH_2Cl_2 (20 mL). After 2 h the solution was added dropwise over *ca*. 30 min to a cooled (−78 °C) and stirred slurry of flash chromatography silica gel (*ca*. 10 g) in CH_2Cl_2 (100 mL). The cooling bath was removed, and when the temperature of the mixture reached 0 °C, water (8 mL) was added. The mixture was filtered through a pad (2 × 6 cm) of Celite, using CH_2Cl_2 as a rinse. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2.5 × 18 cm), using 10% EtOAc−hexane, gave allylic alcohol **57** (349.3 mg, 89%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3348 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (s, 3 H), 1.04 (s, 3 H), 1.11 (dd, J = 7.5, 5.0 Hz, 1 H), 1.26 (d, J = 8.0 Hz, 1 H), 1.32−1.48 (m, 2 H), 1.56 (dd, J = 2.0, 1.0 Hz, 3 H), 1.61 (dd, J = 1.0, 1.0 Hz, 3 H), 1.66 (ddd, J = 7.0, 3.5, 2.0 Hz, 1 H), 2.82−3.06 (m, 2 H), 4.56 (br dd, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 11.21 (q′), 12.69 (q′), 27.61 (q′), 29.13 (q′), 39.89 (t′), 41.85 (s′), 44.42 (d′), 46.19 (t′), 52.95 (d′), 79.75 (d′), 131.07 (s′), 137,70 (s′); exact mass *m*/*z* calcd for $C_{12}H_{20}O$ 180.1514, found 180.1509. An analytical sample was prepared by Kugelrohr distillation (90−100 °C, 0.6 mmHg). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.95; H, 11.32.

(1α,3aα,6aα)-(±)-1,3a,4,5,6,6a-Hexahydro-2,3,5,5-tetramethyl-1-pentalenol (58). Ph_3P (611.1 mg, 2.66 mmol) and chloroacetic acid (251.4 mg, 2.66 mmol) were added successively to a stirred solution of allylic alcohol **57** (240.1 mg, 1.33 mmol) in dry PhH (10 mL) at room temperature. DEAD (0.42 mL, 2.66 mmol) was added dropwise over *ca*. 3 min, and stirring was continued for 3 h. Evaporation of the solution gave a mixture which contained the desired chloro acetate. The mixture was dissolved in THF (10 mL plus 5 mL as a rinse), and this solution was added dropwise over *ca*. 5 min to a cooled (0 °C) and stirred suspension of $LiAlH_4$ (303.2 mg, 8.00 mmol) in THF (25 mL). The cooling bath was removed, and stirring was continued for 30 min. The mixture was then quenched by successive addition of water (0.3 mL), aqueous NaOH (3 M, 0.3 mL), and water (0.9 mL). The resulting mixture was stirred for 20 min and then filtered through a

(39) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972, p 167.

pad (2 × 4 cm) of Celite. The pad was washed with EtOAc, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (2.5 × 15 cm), using 10% EtOAc−hexane, gave allylic alcohol **58** (138.2 mg, 58%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3309, 3295 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93 (s, 3 H), 0.99 (s, 3 H), 0.99 (d J = 11.0 Hz, 1 H), 1.05 (dd, J = 11.0, 10.0 Hz, 1 H), 1.40 (d, J = 7.5 Hz, 1 H), 1.58 (ddd, J = 2.0, 1.5, 1.5 Hz, 3 H), 1.62 (ddd, J = 2.0 Hz, 1 H), 1.64 (ddd, J = 2.0, 1.0, 1.0 Hz, 3 H), 1.78 (ddd, J = 12.0, 8.5, 2.0 Hz, 1 H), 2.5 (dddd, J = 12.0, 10.0, 8.0, 2.0 Hz, 1 H), 3.18 (br ddd, J = 8.0, 8.0, 8.0 Hz, 1 H), 4.19 (br d, J = 8.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 11.41 (q′), 12.86 (q′), 27.30 (q′), 28.71 (q′), 41.47 (s′), 44.82 (t′), 45.87 (t′), 50.95 (d′), 52.76 (d′), 83.38 (d′), 130.38 (s′), 140.68 (s′); exact mass m/z calcd for $C_{12}H_{20}O$ 180.1514, found 180.1510. An analytical sample was prepared by crystallization from hexane: mp 38−39 °C. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.10; H, 11.19.

(1α,3aα,6aα)-(±)-1,3a,4,5,6,6a-Hexahydro-1,2,5,5-tetramethyl-1-pentaleneethanol (61). Use of Ethyl Vinyl Ether. The yield in this experiment was not always reproducible. NaOAc (213.3 mg, 2.60 mmol) and $Hg(OAc)_2$ (414.3 mg, 1.30 mmol) were added to a stirred solution of alcohol **58** (234.5 mg, 1.30 mmol) in freshly distilled ethyl vinyl ether (120 mL). The resulting suspension was refluxed for 72 h and then cooled to room temperature. Anhydrous K_2CO_3 was added, and the excess of ethyl vinyl ether was evaporated. The residue was taken up in 2:3 CH_2Cl_2−hexane and filtered through a pad (2 × 4 cm) of Celite. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2.5 × 20 cm), using 2% EtOAc−hexane, gave the desired vinyl ether (210.2 mg, 78%) as a colorless oil containing trace impurities (^{1}H NMR, 200 MHz): FTIR (film) 2951, 2930, 2866, 1644, 1629, 1603, 1463, 1442, 1382, 1366, 1158 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.94 (s, 3 H), 1.02 (s, 3 H), 1.02 (d, J = 13.0 Hz, 1 H), 1.14 (dd, J = 13.0, 10.0 Hz, 1 H), 1.55−1.64 (m, 6 H), 1.64 (ddd, J = 13.0, 9.0, 2.0 Hz, 1 H), 1.78 (ddd, J = 13.0, 8.0, 2.0 Hz, 1 H), 2.6 (dddd, J = 9.0, 9.0, 8.0, 2.0 Hz, 1 H), 3.2 (br ddd, J = 8.0, 8.0, 8.0 Hz, 1 H), 4.00 (dd, J = 7.0, 1.5 Hz, 1 H), 4.23 (dd, J = 14.0, 1.5 Hz, 1 H), 4.37 (br s, 1 H), 6.41 (ddd, J = 14.0, 7.0, 1.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 11.71 (q′), 12.88 (q′), 27.18 (q′), 28.70 (q′), 41.71 (s′), 45.05 (t′), 45.96 (t′), 46.93 (d′), 52.23 (d′), 87.74 (t′), 93.90 (d′), 127.44 (s′), 142.99 (s′), 150.85 (d′); exact mass m/z calcd for $C_{14}H_{22}O$ 206.1671, found 206.1670.

i-Bu_3Al (1.0 M in PhMe, 3.9 mL, 3.9 mmol) was added to a cooled (−78 °C) and stirred solution of the above vinyl ether (201.0 mg, 0.974 mmol) in CH_2Cl_2 (15 mL). The cold bath was removed, and after 1.5 h, the solution was cooled to −78 °C and quenched by addition of hydrochloric acid (1 M, 2 mL). The resulting mixture was poured into a separatory funnel containing 1 M hydrochloric acid (50 mL) and EtOAc (50 mL). The layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2.5 × 17 cm), using 20% EtOAc−hexane, gave alcohol **61** (186.1 mg, 91%) as a pure (^{1}H NMR, 200 MHz) colorless oil: FTIR (CH_2Cl_2 cast) 3324 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (s, 3 H), 0.95 (s, 3 H), 1.01 (s, 3 H), 1.04 (dd, J = 13.0, 7.0 Hz, 1 H), 1.27 (dd, J = 2.0, 2.0 Hz, 1 H), 1.32 (d, 1.5 Hz, 1 H), 1.35 (dd, J = 6.0, 6.0 Hz, 1 H), 1.58 (ddd J = 1.5, 1.5, 1.5 Hz, 3 H), 1.61−1.71 (m, 3 H), 2.60 (ddd, J = 11.0, 8.0, 7.0 Hz, 1 H), 2.96−3.14 (m, 1 H), 3.65 (ddd, J = 7.5, 7.0, 6.0 Hz, 2 H), 5.18 (dd, J = 1.5, 1.5 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 12.54 (q′), 21.31 (q′), 27.46 (q′), 29.30 (q′), 40.49 (s′), 43.02 (t′), 44.53 (t′), 46.46 (t′), 47.22 (d′), 48.87 (s′), 51.67 (d′), 60.55 (t′), 129.57 (d′), 143.14 (s′); exact mass m/z calcd for $C_{14}H_{24}O$ 208.1827, found 208.1829. An analytical sample was prepared by Kugelrohr distillation (68−70 °C, 1.5 mmHg). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.52; H, 11.68.

(1α,3aα,6aα)-(±)-1,3a,4,5,6,6a-Hexahydro-1,2,5,5-tetramethyl-1-pentaleneethanol (61). Use of Phenyl Vinyl Sulfoxide. Alcohol **58** (540.8 mg, 3.00 mmol) in THF (5 mL plus 1 mL as a rinse) was added to a stirred suspension of NaH (72.0 mg, 3.00 mmol) in THF (5 mL) at room temperature. Stirring was continued for 30 min, and then a solution of phenyl vinyl sulfoxide (0.53 mL, 4.00 mmol) in THF (2 mL) and a catalytic amount (1 mg) of KH were added. The mixture was stirred for 4 h and then quenched by addition of moist EtOAc followed by water. The layers were separated, and the aqueous phase was extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. The residue was dissolved in decalin (10 mL), and $NaHCO_3$ (10 g) was added. The resulting mixture was heated (150 °C) and stirred for 40 h and then cooled to room temperature. Water was added, and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2.5 × 20 cm), using first hexane and then 10% EtOAc−hexane, gave crude (TLC, 20% EtOAc−hexane) aldehyde **60**, which was used without further purification.

All of the crude **60** in THF (3 mL plus 2 mL as a rinse) was added to a stirred and cooled (−78 °C) suspension of $LiAlH_4$ (79.9 mg, 2.00 mmol) in THF (15 mL). The cold bath was removed, the mixture was allowed to warm to room temperature (30 min), and the reaction was quenched by successive addition of water (0.08 mL), aqueous NaOH (3 M, 0.08 mL), and water (0.24 mL). The resulting mixture was stirred for 20 min and then filtered through a pad (3 × 3 cm) of Celite. The pad was washed with EtOAc, and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (2.5 × 15 cm), using 20% EtOAc−hexane, gave alcohol **61** (453.6 mg, 73%) as a pure (^{1}H NMR, 200 MHz), colorless oil, spectroscopically identical with material made using ethyl vinyl ether.

(1α,3aα,6aα)-(±)-1-(2-Bromoethyl)-1,3a,4,5,6,6a-hexahydro-1,2,5,5-tetramethylpentalene (62). Ph_3P (786.9 mg, 3.00 mmol) and CBr_4 (995.0 mg, 3.00 mmol) were added successively to a cooled (0 °C) and stirred solution of alcohol **61** (443.6 mg, 2.13 mmol) in CH_2Cl_2 (40 mL). The cold bath was removed, and after 1.5 h, the mixture was filtered through a pad (3 × 3 cm) of flash chromatography silica gel, using CH_2Cl_2. Evaporation of the filtrate and flash chromatography of the residue over silica gel (3.5 × 25 cm), using petroleum ether, gave bromide **62** (551.6 mg, 96%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3027, 2952, 2932, 2865, 2857, 1462, 1445, 1381, 1371, 1365 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (s, 3 H), 0.95 (s, 3 H), 1.02 (s, 3 H), 1.04 (dd, J = 13.0, 7.0 Hz, 1 H), 1.20−1.38 (m, 2 H), 1.54 (dd, J = 2.0, 1.0 Hz, 3 H), 1.63 (ddd, J = 13.0, 9.5, 2.0 Hz, 1 H), 1.81−2.06 (m, 2 H), 2.53 (ddd, J = 13.0, 8.0, 7.0 Hz, 1 H), 2.90−3.09 (m, 1 H), 3.17−3.46 (m, 2 H), 5.21 (dd, J = 1.0, 1.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 12.44 (q′), 20.72 (q′), 27.46 (q′), 29.27 (q′), 29.99 (t′), 40.56 (s′), 42.99 (t′), 45.47 (t′), 46.40 (t′), 47.31 (d′), 51.15 (d′), 51.21 (s′), 130.15 (d′), 141.18 (s′); exact mass m/z calcd for $C_{14}H_{23}Br$ 270.0984, found 270.0982. An analytical sample was prepared by Kugelrohr distillation (82−85 °C, 1.5 mmHg). Anal. Calcd for $C_{14}H_{23}Br$: C, 61.99; H, 8.55; Br, 29.46. Found C, 61.66; H, 8.83; Br, 29.71.

(1α,3aα,6aα)-(±)-1-(3-Butynyl)-1,3a,4,5,6,6a-hexahydro-1,2,5,5-tetramethylpentalene (64). *n*-BuLi (1.6 M in hexane, 3.13 mL, 5.00 mmol) was added dropwise over *ca.* 5 min to a cooled (−78 °C) and stirred solution of (trimethylsilyl)-acetylene (1.41 mL, 10.0 mmol) in THF (15 mL). After a further 15 min, a solution of bromide **62** (267.0 mg, 0.984 mmol) in THF (5 mL plus 3 mL as a rinse) followed by HMPA (1 mL) were added. The cold bath was removed, and stirring was continued for 6 h. Methanolic NaOH (1 M, 15 mL) was added, and stirring was continued overnight. The mixture was quenched with water and extracted with hexane. The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2.5 × 15 cm), using petroleum ether, gave enyne **64** (199.6 mg, 94%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (film) 3313, 3027, 2952, 2934, 2867, 2119, 1463, 1447, 1440, 1380, 1374, 1365 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (s, 3 H), 0.93 (s, 3 H), 1.01 (s, 3 H), 1.02 (dd, J = 13.0, 7.5 Hz, 1 H), 1.17−1.33 (m, 2 H), 1.47−1.74 (m, 3 H), 1.53 (dd, J = 3.0, 1.5 Hz, 3 H), 1.92 (dd, J = 2.5, 2.5 Hz, 1 H), 2.01−2.16 (m, 2 H), 2.52 (ddd, J = 10.0, 9.0, 8.0 Hz, 1 H), 2.89−3.08 (m, 1 H), 5.21 (dd, J =

1.5, 1.5 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 12.39 (q′), 13.99 (t′), 20.71 (q′), 27.41 (q′), 29.28 (q′), 40.53 (s′), 40.64 (t′), 43.09 (t′), 46.48 (t′), 47.22 (d′), 49.89 (s′), 50.94 (d′), 67.63 (d′), 85.64 (s′), 129.88 (d′), 141.67 (s′); exact mass *m*/*z* calcd for $C_{16}H_{24}$ 216.1878, found 216.1870. An analytical sample was prepared by Kugelrohr distillation (85−90 °C, 1.7 mmHg). Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.65; H, 11.12.

(1*R,2*R**,6*S**,7*R**)-(±)-1,4,4,11-Tetramethyl-8-methylenetricyclo[5,3,1,0^{2,6}]undecane (66).** Bu_3SnH (0.11 mL, 0.42 mmol) in PhMe (1 mL) was added to a warmed (80 °C) and stirred solution of enyne **64** in PhMe (5 mL). AIBN (3.4 mg, 0.021 mmol) was added, and stirring was continued for 3 h. The mixture was then cooled and evaporated. Flash chromatography of the residue over silica gel (1.5 × 30 cm), using petroleum ether, gave a mixture (^{1}H NMR, 200 MHz) of olefin **66** and a byproduct (35.4 mg, *ca*. 78%, 5:1 in favor of **66**).

A sample of **66**, containing only trace impurities, was obtained by repeated flash chromatography, in which late fractions were discarded. This material had: FTIR (neat film) 3068, 2950, 2930, 2870, 2857, 1648, 1464, 1438, 1381, 1373, 1365 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 0.75 (d, J = 7.0 Hz, 3 H), 0.76 (s, 3 H), 0.90−1.24 (m, 3 H), 0.92 (s, 3 H), 1.05 (s, 3 H), 1.29−1.86 (m, 4 H), 1.95−2.10 (m, 2 H), 2.15−2.42 (m, 3 H), 4.45 (dd, J = 2.5, 2.5 Hz, 1 H), 4.55 (dd, J = 2.5, 2.5 Hz, 1 H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 10.06 (q′), 21.03 (q′), 26.44 (q′), 28.75 (q′), 28.91 (t′), 34.46 (t′), 39.24 (d′), 40.38 (s′), 41.70 (s′), 44.31 (t′), 46.34 (d′), 47.65 (t′), 51.92 (d′), 55.68 (d′), 105.93 (t′), 150.66 (s′); exact mass *m*/*z* calcd for $C_{16}H_{26}$ 218.20344, found 218.20302.

(1aα,2aα,5aα)- and (1aα,2*β*,2a*β*,5a*β*)-(±)-2-(3-Butynyl)-1a,2,4,4-tetramethyloctahydropenteno[1,2-*b*]oxirene (80α) and (80*β*). $NaH_2PO_4 \cdot H_2O$ (567.8 mg, 4.00 mmol) and *m*-CPBA (552.2 mg, 3.20 mmol) were added to a cooled (0 °C) and stirred solution of enyne **64** (347.9 mg, 1.61 mmol) in CH_2Cl_2 (60 mL). The mixture was stirred for 3 h, and then the cold bath was removed. Additional CH_2Cl_2 (40 mL) was added, and the organic layer was washed successively with water, saturated aqueous $NaHCO_3$, and brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2.5 × 25 cm), using 5% EtOAc−hexane, gave epoxide **80**α (281.6 mg, 75%) as a pure (^{1}H NMR, 200 MHz), colorless oil and then epoxide **80***β* (95.2 mg, 25%) as a white solid containing trace aromatic impurities (^{1}H NMR, 200 MHz). The stereochemical assignments to **80**α and **80***β* were made on the basis of NOE measurements on the derived ketone **85***β* (see later).

Major diastereomer **80**α: FTIR (CH_2Cl_2 cast) 3312, 2953, 2935, 2863, 2119, 1773, 1462, 1442, 1417, 1374, 1366 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.86 (s, 3 H), 0.95 (s, 3 H), 1.02 (s, 3 H), 1.12 (ddd, J = 11.0, 8.0, 1.5 Hz, 1 H), 1.25 (s, 3 H), 1.29−1.69 (m, 5 H), 1.98 (dd, J = 2.5, 2.5 Hz, 1 H), 2.03−2.30 (m, 2 H), 2.34 (ddd, J = 12.0, 9.0, 7.5 Hz, 1 H), 2.55 (dddd, J = 9.0, 7.5, 7.5, 2.0 Hz, 1 H), 3.09 (d, J = 2.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 14.12 (t′), 14.22 (q′), 17.23 (q′), 27.45 (q′), 29.09 (q′), 40.19 (t′), 41.44 (t′), 41.76 (s′), 43.33 (d′), 44.80 (s′ and t′ overlapping), 50.42 (d′), 68.16 (d′), 68.86 (d′), 73.07 (s′), 85.18 (s′); exact mass *m*/*z* calcd for $C_{16}H_{24}O$ 232.18270, found 232.18325.

Minor diastereomer **80***β*: FTIR (CH_2Cl_2 cast) 3311, 2953, 2933, 2865, 2118, 1772, 1468, 1428, 1419, 1383, 1374, 1366 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.89 (s, 3 H), 0.95 (s, 3 H), 1.04 (s, 3 H), 1.06 (dd, J = 12.0, 12.0 Hz, 1 H), 1.29 (s, 3 H), 1.33−1.77 (m, 5 H), 1.94−2.27 (m, 3 H), 1.95 (dd, J = 2.5, 2.5 Hz, 1 H), 2.73 (ddd, J = 12.0, 9.0, 7.5 Hz, 1 H), 3.12 (s, 1 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 14.49 (t′), 15.16 (q′), 21.11 (q′), 28.90 (q′), 29.36 (q′), 37.77 (t′), 41.76 (t′), 42.09 (s′), 43.18 (t′), 44.32 (s′), 46.75 (d′), 50.30 (d′), 67.04 (d′), 67.96 (d′), 71.65 (s′), 85.55 (s′); exact mass *m*/*z* calcd for $C_{16}H_{24}O$ 232.18270, found 232.18129.

(3aα,3b*β*,6a*β*,7α,7aα)-(±)-Decahydro-3a,5,5,7a-tetramethyl-1-methylene-(1*H*)-cyclopenta[*a*]pentalen-7-ol (83α). $TiCp_2Cl$ (939.6 mg, 4.40 mmol) in THF (44 mL) was added dropwise over *ca*. 5 min to a stirred solution of epoxide **80**α (466.3 mg, 2.01 mmol) in THF (30 mL). Stirring was continued overnight, and then the mixture was quenched by addition of 10% H_2SO_4 (100 mL). The aqueous phase was extracted with EtOAc, and the combined organic fractions were washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2.5 × 15 cm), using 5% EtOAc−hexane, gave alcohol **83**α (387.6 mg, 82%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3491 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.92 (s, 3 H), 0.94 (s, 3 H), 1.00 (s, 3 H), 1.07 (s, 3 H), 1.22−1.66 (m, 7 H), 2.27−2.57 (m, 3 H), 2.78 (dddd J = 9.0, 7.0, 5.0, 5.0 Hz, 1 H), 3.84 (dd, J = 7.0, 5.0 Hz, 1 H), 4.74 (ddd, J = 2.5, 2.5, 1.0 Hz, 1 H), 4.84 (ddd, J = 2.5, 2.5, 1.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 16.90 (q′), 20.02 (q′), 27.42 (q′), 29.37 (q′), 30.66 (t′), 40.04 (t′), 40.28 (t′), 41.64 (s′), 43.96 (t′), 46.64 (d′), 51.78 (s′), 53.17 (d′), 61.14 (s′), 81.41 (d′), 104.77 (t′), 162.40 (s′); exact mass *m*/*z* calcd for $C_{16}H_{26}O$ 234.19836, found 234.19762. Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.98; H, 11.37.

(3aα,3b*β*,6a*β*,7*β*,7aα)-(±)-Decahydro-3a,5,5,7a-tetramethyl-1-methylene-(1*H*)-cyclopenta[*a*]pentalen-7-ol (83*β*). $TiCp_2Cl$ (140.9 mg, 0.660 mmol) in THF (6.6 mL) was added dropwise over *ca*. 4 min to a stirred solution of epoxide **80***β* (75.3 mg, 0.324 mmol) in THF (6 mL). Stirring was continued for 1.5 h, and then the mixture was quenched by addition of 10% H_2SO_4 (12 mL). The aqueous phase was extracted with EtOAc, and the combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 15 cm), using 5% EtOAc−hexane, gave alcohol **83***β* (61.7 mg, 81%) as a pure (^{1}H NMR, 200 MHz), white solid: FTIR (CH_2Cl_2 cast) 3441 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.90 (s, 3 H), 0.94 (s, 3 H), 1.00 (s, 3 H), 1.07 (s, 3 H), 1.24−1.56 (m, 5 H), 1.56−1.76 (m, 2 H), 2.04 (dddd, J = 9.0, 9.0, 8.0, 5.5 Hz, 1 H), 2.21−2.50 (m, 3 H), 3.36 (dd, J = 9.0, 9.0 Hz, 1 H), 4.80 (ddd, J = 1.5, 1.0, 1.0 Hz, 1 H), 5.04 (ddd, J = 1.5, 1.0, 1.0 Hz, 1 H); ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 20.32 (q′), 20.84 (q′), 27.67 (q′), 29.54 (q′), 33.17 (t′), 41.30 (s′), 41.47 (t′), 43.69 (t′), 45.30 (t′), 50.40 (s′), 50.67 (d′), 52.13 (d′), 59.23 (s′), 87.60 (d′), 106.91 (t′), 158.90 (s′); exact mass *m*/*z* calcd for $C_{16}H_{26}O$ 234.19836, found 234.19728. An analytical sample was prepared by crystallization from hexane: mp 50−52 °C. Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.88; H, 11.31.

Acetic acid (3aα,3b*β*,6a*β*,7α,7aα)-(±)-Decahydro-3a,5,5,7a-tetramethyl-1-methylene-(1*H*)-cyclopenta[*a*]pentalen-7-yl Ester (84α). Pyridine (97 μL, 1.2 mmol), Ac_2O (0.11 mL, 1.2 mmol), AcCl (85 μL, 1.2 mmol), and DMAP (8.5 mg, 0.070 mmol) were added successively to a stirred solution of alcohol **83**α (76.7 mg, 0.328 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred and refluxed for 1 h, allowed to cool to room temperature, diluted with EtOAc (30 mL), washed with water and brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 15 cm), using 5% EtOAc−hexane, gave ester **84**α (85.1 mg, 95%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 1740 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.91 (s, 3 H), 0.95 (s, 6 H), 1.05 (s, 3 H), 1.14−1.74 (m, 6 H), 2.06 (s, 3 H), 2.27−2.61 (m, 3 H), 2.83 (dddd, J = 10.0, 8.0, 8.0, 6.5 Hz, 1 H), 4.84 (dd, J = 2.5, 2.5 Hz, 1 H), 4.90 (ddd, J = 2.5, 2.5, 1.0 Hz, 1 H), 4.95 (d, J = 6.5 Hz, 1 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 18.20 (q′), 20.13 (q′), 21.18 (q′), 27.71 (q′), 29.55 (q′), 30.72 (t′), 40.12 (t′), 40.23 (t′), 41.93 (s′), 43.55 (t′), 45.85 (d′), 52.00 (s′), 53.71 (d′), 60.71 (s′), 84.37 (d′), 106.16 (t′), 161.26 (s′), 170.73 (s′); exact mass *m*/*z* calcd for $C_{18}H_{28}O_2$ 276.20892, found 276.20853.

Acetic acid (3aα,3b*β*,6a*β*,7*β*,7aα)-(±)-Decahydro-3a,5,5,7a-tetramethyl-1-methylene-(1*H*)-cyclopenta[*a*]pentalen-7-yl ester (84*β*). Pyridine (49 μL, 0.60 mmol), Ac_2O (57 μL, 0.60 mmol), AcCl (43 μL, 0.60 mmol), and DMAP (6.1 mg, 0.050 mmol) were added successively to a stirred solution of alcohol **83***β* (66.5 mg, 0.284 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 1.5 h, diluted with EtOAc (30 mL), washed with water and brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 15 cm), using 5% EtOAc−hexane, gave ester **84***β* (74.6 mg, 95%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 1739 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ

0.89 (s, 3 H), 0.91 (s, 3 H), 1.03 (s, 3 H), 1.07 (s, 3 H), 1.24−1.52 (m, 3 H), 1.54 (d, J = 4.0 Hz, 1 H), 1.61−1.77 (m, 2 H), 1.99 (s, 3 H), 2.24−2.63 (m, 4 H), 4.75−4.85 (m, 2 H), 4.94 (ddd, J = 2.0, 2.0, 1.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 19.89 (q′), 21.46 (q′), 21.63 (q′), 27.22 (q′), 29.50 (q′), 32.27 (t′), 40.15 (t′), 42.19 (s′), 43.58 (t′), 46.47 (t′), 48.70 (d′), 52.43 (d′), 52.48 (s′), 59.87 (s′), 88.98 (d′), 107.56 (t′), 158.19 (s′), 170.71 (s′); exact mass m/z calcd for $C_{18}H_{28}O_2$ 276.20892, found 276.20806.

(3aα,3b*β*,6a*β*,7α,7aα)-(±)-Decahydro-7-hydroxy-3a,5,5,7a-tetramethylcyclopenta[*e*]pentalen-1-one (85α). OsO_4 (2.5 w/w % in 2-methyl-2-propanol, 1.27 mL, 0.100 mmol) was added dropwise to a stirred solution of olefinic acetate **84**α (180.3 mg, 0.652 mmol) in acetone (5 mL) and water (0.5 mL). 4-Methylmorpholine *N*-oxide monohydrate (210.9 mg, 1.80 mmol) was added in one portion, and stirring was continued for 24 h. The mixture was filtered through a pad (1.5 × 6 cm) of Celite on top of a pad (1.5 × 7 cm) of flash chromatography silica gel, using EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.5 × 20 cm), using 50% EtOAc−hexane, gave the desired diols (173.1 mg, 85%) as a mixture (TLC) of diastereomers, which was used without further purification.

K_2CO_3 (414.6 mg, 3.00 mmol) was added to a stirred solution of the above diols in MeOH (8 mL), and stirring was continued for 2 h. The MeOH was evaporated, the flask was flushed with argon, and CH_2Cl_2 (8 mL) was added. The mixture was cooled (0 °C), and $Pb(OAc)_4$ (532.0 mg, 1.20 mmol) was added. The resulting mixture was stirred for 15 min, the cold bath was removed, and stirring was continued for 20 min. The mixture was then filtered through a pad (2 × 3 cm) of flash chromatography silica gel, using EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.5 × 20 cm), using 20% EtOAc−hexane, gave ketone **85**α (123.6 mg, 80% from **84**α) as a pure (^{1}H NMR, 200 MHz), white solid: FTIR (CH_2Cl_2 cast) 1728 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.93 (s, 3 H), 0.97 (s, 3 H), 0.98 (s, 3 H), 1.08 (s, 3 H), 1.25−1.85 (m, 7 H), 2.13−2.48 (m, 2 H), 2.51 (ddd, J = 10.0, 10.0, 9.5 Hz, 1 H), 2.77 (dddd, J = 10.0, 10.0, 9.5, 7.5 Hz, 1 H), 4.03 (dd, J = 7.5, 5.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 12.07 (q′), 19.89 (q′), 26.99 (q′), 29.20 (q′), 35.51 (t′), 40.16 (t′, t′ overlapping), 41.65 (s′), 43.83 (t′), 47.67 (d′), 49.89 (s′), 53.79 (d′), 65.04 (s′), 77.00 (d′), 222.72 (s′); exact mass m/z calcd for $C_{15}H_{24}O_2$ 236.17763, found 236.17668. An analytical sample was prepared by crystallization from hexane: mp 81−82 °C. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.08; H, 10.52.

(3aα,3b*β*,6a*β*,7*β*,7aα)-(±)-Decahydro-7-hydroxy-3a,5,5,7a-tetramethylcyclopenta[*e*]pentalen-1-one (85*β*). OsO_4 (2.5 w/w % in 2-methyl-2-propanol, 0.70 mL, 0.055 mmol) was added dropwise to a stirred solution of olefinic acetate **84***β* (99.3 mg, 0.359 mmol) in acetone (3 mL) and water (0.25 mL). 4-Methylmorpholine *N*-oxide monohydrate (117.2 mg, 1.00 mmol) was added in one portion, and stirring was continued for 24 h. The mixture was filtered through a pad (1.5 × 6 cm) of Celite on top of a pad (1.5 × 7 cm) of flash chromatography silica gel, using EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.5 × 15 cm), using 50% EtOAc−hexane, gave the desired diols (95.8 mg, 86%) as a mixture (TLC) of diastereomers, which was used without further purification.

K_2CO_3 (248.8 mg, 1.80 mmol) was added to a stirred solution of the above diols in MeOH (5 mL), and stirring was continued for 2 h. The MeOH was evaporated, the flask was flushed with argon, and CH_2Cl_2 (5 mL) was added. The mixture was cooled (0 °C), and $Pb(OAc)_4$ (310.4 mg, 0.700 mmol) was added. The resulting mixture was stirred for 15 min, the cold bath was removed, and stirring was continued for 20 min. The mixture was then filtered through a pad (2 × 3 cm) of flash chromatography silica gel, using EtOAc. Evaporation of the filtrate and flash chromatography of the residue over silica gel (1.5 × 20 cm), using 20% EtOAc−hexane, gave ketone **85***β* (63.8 mg, 75% from **84***β*) as a pure (^{1}H NMR, 200 MHz), white solid: FTIR (CH_2Cl_2 cast) 1716 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.90 (s, 3 H), 0.96 (s, 3 H), 1.00 (s, 3 H), 1.06 (s, 3 H), 1.22 (dd, J = 10.0, 7.0 Hz, 1 H), 1.30−1.48 (m, 2 H), 1.59−2.01 (m, 3 H), 2.11−2.44 (m, 3 H), 2.55 (ddd, J = 11.0, 11.0, 8.5 Hz, 1 H), 2.88 (d, J = 8.5 Hz, 1 H), 3.54 (dd, J = 8.5, 8.5 Hz, 1 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 16.03 (q′), 20.29 (q′), 27.32 (q′), 29.45 (q′), 35.57 (t′), 37.20 (t′), 42.78 (s′), 43.18 (t′), 46.79 (t′), 48.76 (s′), 51.73 (d′), 52.26 (d′), 62.98 (s′), 88.63 (d′), 227.40 (s′); exact mass m/z calcd for $C_{15}H_{24}O_2$ 236.17763, found 236.17678. An analytical sample was prepared by crystallization from hexane: mp 92−93 °C. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 75.91; H, 10.04.

Irradiation of the C(7)H signal in the proton NMR spectrum caused an enhancement of 8% in the signal intensity of one of the C(6) hydrogens, as expected on the basis of the stereochemistry assigned to **85***β*.

Thiocarbonic Acid *O*-Phenyl *O*-[(3aα,3b*β*,6a*β*,7α,7aα)-(±)-Decahydro-3a,5,5,7a-tetramethyl-1-oxo-(1*H*)-cyclopenta[*e*]pentalen-7-yl] Ester (86α). DMAP (488.3 mg, 4.00 mmol) and phenyl chlorothionoformate (0.41 mL, 3.0 mmol) were added successively to a stirred solution of alcohol **85**α (154.2 mg, 0.652 mmol) in MeCN (7 mL). Stirring was continued for 24 h. The mixture was quenched with water and extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 25 cm), using 10% EtOAc−hexane, gave thionocarbonate **86**α (204.3 mg, 84%) as a pure (^{1}H NMR, 200 MHz), white solid: FTIR (CH_2Cl_2 cast) 2953, 2867, 1738, 1591, 1490, 1465, 1457, 1408, 1384, 1366, 1244, 1199 cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.93 (s, 3 H), 0.95 (s, 3 H), 0.99 (s, 3 H), 1.10 (s, 3 H), 1.29−1.53 (m, 4 H), 1.62−1.95 (m, 2 H), 2.23−2.55 (m, 2 H), 2.57 (ddd, J = 10.0, 10.0, 10.0 Hz, 1 H), 2.97 (dddd, J = 10.0, 10.0, 9.0, 7.0 Hz, 1 H), 5.59 (d, J = 7.0 Hz, 1 H), 7.06−7.16 (m, 2 H), 7.24−7.50 (m, 3 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 13.01 (q′), 19.73 (q′), 27.11 (q′), 29.21 (q′), 34.65 (t′), 35.15 (t′), 40.38 (t′), 42.32 (s′), 43.00 (t′), 46.69 (d′), 49.67 (s′), 53.49 (d′), 65.16 (s′), 90.12 (d′), 122.24 (d′), 126.92 (d′), 129.94 (d′), 153.74 (s′), 194.83 (s′), 220.67 (s′); exact mass m/z calcd for $C_{15}H_{23}O$ (M − $C_7H_5O_2S$) 219.17488, found 219.17448.

Thiocarbonic Acid *O*-Phenyl *O*-[(3aα,3b*β*,6a*β*,7*β*,7aα)-(±)-Decahydro-3a,5,5,7a-tetramethyl-1-oxo-(1*H*)-cyclopenta[*e*]pentalen-7-yl] Ester (86*β*). DMAP (195.3 mg, 1.60 mmol) and phenyl chlorothionoformate (0.17 mL, 1.2 mmol) were added successively to a stirred solution of alcohol **85***β* (56.7 mg, 0.240 mmol) in MeCN (3 mL). Stirring was continued for 24 h. The mixture was quenched with water and extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 20 cm), using 10% EtOAc−hexane, gave thionocarbonate **86***β* (66.3 mg, 74%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2952, 2864, 1741, 1591, 1490, 1466, 1456, 1406, 1384, 1366, 1292, 1280, 1220, 1200, cm^{-1}; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.92 (s, 3 H), 0.94 (s, 3 H), 1.08 (s, 3 H), 1.11 (s, 3 H), 1.25−1.57 (m, 3 H), 1.67−2.27 (m, 5 H), 2.71−3.00 (m, 2 H), 5.12 (d, J = 1.5 Hz, 1 H), 7.01−7.13 (m, 2 H), 7.23−7.47 (m, 3 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 17.97 (q′), 18.58 (q′), 26.14 (q′), 29.03 (q′), 35.94 (t′), 37.24 (t′), 41.48 (s′), 44.42 (t′), 48.28 (t′), 51.25 (d′), 53.01 (s′), 55.50 (d′), 63.75 (s′), 100.92 (d′), 122.25 (d′), 126.87 (d′), 129.94 (d′), 153.63 (s′), 193.80 (s′), 218.59 (s′); exact mass m/z calcd for $C_{15}H_{23}O$ (M − $C_7H_5O_2S$) 219.17488, found 219.17451.

(3aα,3b*β*,6a*β*,7aα)-(±)-Decahydro-3a,5,5,7a-tetra-methylcyclopenta[*e*]pentalen-1-one (87) from 86α. Et_3B (1.0 M in pentane, 0.14 mL, 0.14 mmol) was added dropwise to a cooled (0 °C) and stirred solution of thionocarbonate **86**α (54.2 mg, 0.145 mmol) and Bu_3SnH (0.16 mL, 0.58 mmol) in hexane (3 mL). Air (20 mL) was injected into the flask, and stirring was continued for 1 h, at which point reaction was still incomplete (TLC control, silica, 10% EtOAc−hexane). Evaporation of the solvent and flash chromatography of the residue over silica gel (1.0 × 10 cm), using 5% EtOAc−hexane, gave mixed fractions of starting material and product. Fractions containing starting material and/or product were combined and evaporated. The residue was resubjected to the original reaction conditions, and after 1 h, all starting material had been consumed (TLC control, above system). Evaporation of the solvent and flash chromatography of the residue over

silica gel (1.0 × 20 cm), using 5% EtOAc−hexane, gave ketone **87** (23.2 mg, 72%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2948, 2865, 1737, 1466, 1451, 1382, 1366; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.90 (s, 3 H), 0.95 (s, 3 H), 1.01 (s, 3 H), 1.06 (s, 3 H), 1.07−1.30 (m, 2 H), 1.41 (br d, J = 9.0 Hz, 2 H), 1.60−1.83 (m, 3 H), 1.98−2.73 (m, 5 H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 18.05 (q′), 18.93 (q′), 26.93 (q′), 29.45 (q′), 34.81 (t′), 35.38 (t′), 42.14 (d′), 42.41 (s′), 43.58 (t′), 43.62 (t′), 49.82 (t′), 51.70 (s′), 56.18 (d′), 61.30 (s′), 223.23 (s′); exact mass m/z calcd for $C_{15}H_{24}O$ 220.18271, found 220.18280.

(3aα,3bβ,6aβ,7aα)-(±)-Decahydro-3a,5,5,7a-tetra-methylcyclopenta[*e*]pentalen-1-one (87) from 86β. Et_3B (1.0 M in pentane, 0.18 mL, 0.18 mmol) was added dropwise to a cooled (0 °C) and stirred solution of thionocarbonate **86**β (68.6 mg, 0.184 mmol) and Bu_3SnH (0.20 mL, 0.74 mmol) in hexane (4 mL). Air (20 mL) was injected into the flask, and stirring was continued for 1 h, at which point reaction was incomplete (TLC control, silica, 10% EtOAc−hexane). Evaporation of the solvent and flash chromatography of the residue over silica gel (1.0 × 10 cm), using 5% EtOAc−hexane, gave mixed fractions of starting material and product. Fractions containing starting material and/or product were combined and evaporated. The residue was resubjected to the original reaction conditions, and after 1 h, all starting material had been consumed (TLC control, above system). Evaporation of the solvent and flash chromatography of the residue over silica gel (1.0 × 20 cm), using 5% EtOAc−hexane, gave ketone **87** (29.8 mg, 73%) as a pure (^{1}H NMR, 200 MHz), colorless oil, spectroscopically identical to material obtained in the previous experiment.

(1α,3aβ,3bα,6aα,7aβ)-(±)-Decahydro-3a,5,5,7a-tetramethyl-(1*H*)-cyclopenta[*e*]pentalen-1-ol [(±)-Ceratopicanol] (54). $NaBH_4$ (29.1 mg, 0.768 mmol) was added to a cooled (−20 °C) and stirred solution of ketone **87** (56.4 mg, 0.256 mmol) in MeOH (10 mL). Stirring was continued for 20 min, and then the mixture was quenched with water, allowed to warm to room temperature, and extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 20 cm), using 20% EtOAc−hexane, gave alcohol **54** (46.3 mg, 81%) as a pure (^{1}H NMR, 200 MHz), white solid: mp 67−68 °C; exact mass calcd for $C_{15}H_{26}O$ 222.19836, found 222.19828. The ^{1}H NMR[22] and ^{13}C NMR[21] spectra corresponded with the reported data.

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Supporting Information Available: Experimental procedures for the preparation of compounds **69**, **70a**,**b**, **72a**,**b**, **73a**,**b**, **75a**,**b**, **76a**,**b**, and **77a**,**b** and NMR spectra for compounds for which elemental analyses were not obtained (38 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.

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