CH_3 signals that would be observed with θ mis-set from a pulse angle of $\pi/2$ radians. As well, note the sensitivity of the position of maximum enhancement to the setting of the ^1H excitation frequency. We readily conclude that the $^{13}C,^1H$ chemical-shift correlations in ppm for aliphatic CH-type carbons are as follows: C3 (72.8, 3.5), C8 (33.1, 1.4), C9 (51.4, 0.8), C14 (58.0, 1.0), C17 (57.4, 1.1), C20 (37.0, 1.4), and C25 (29.2, 1.5). A useful variation for implementing sequence A is as follows: Because of the functional dependence of the signal intensity with θ, if θ is set equal to $(3\pi)/4$, CH and CH_3 signals will appear in phase, while CH_2 signals will appear phase inverted. A subset of chemical-shift correlation spectra for cholesterol determined with θ set equal to $(3\pi)/4$ are shown in Figure 2. It is probable that this variation will be the method of choice for the implementation of sequence A as not only are the chemical-shift correlations generated but a degree of multiplicity determination is achieved as well. Of course the only ambiguity remaining is the differentiation between CH and CH_3 carbon resonances; this is readily resolved if a hard-pulse version of DEPT is used to determine a complete CH subspectrum; that is, θ is set equal to $\pi/2$ in sequence B.

The major advantages of the selective DEPT sequence are as follows: (1) As no second Fourier transformation is required, the technique is faster in terms of data processing time than existing heteronuclear 2D chemical-shift correlation procedures. (2) Because a selective position of the ^1H spectrum can be interrogated, there can be a significant time saving over existing 2D procedures. For example, when NMR is applied for structure determination of a complex natural product, often all that might be required, or indeed useful, is to generate chemical-shift correlations for selected resolved proton resonances. This is a trivial matter using the above procedure and can be carried out by recording only a few ^{13}C spectra. Although other tecniques, such as selective decoupling or DANTE-induced selective population inversion,[6] are available for this purpose, the spectral quality is often much poorer.

Acknowledgment. This research is supported by the Australian Research Grants Scheme.

Registry No. Cholesterol, 57-88-5.

(6) Canet, D.; Brondequ, J. *J. Magn. Reson.* **1982**, *47*, 159-163.

Synthesis of the Alleged Structure of Senoxydene, the Triquinane Sesquiterpene Derived from *Senecio oxyodontus*

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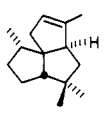
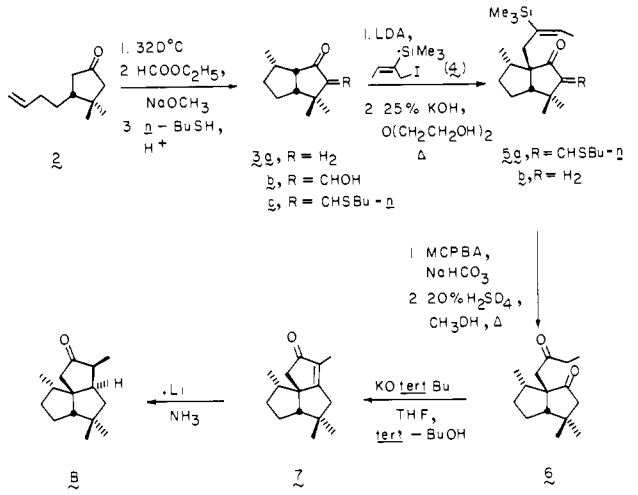
Senoxydene, a sesquiterpene hydrocarbon isolated by Bohlmann and Zdero in 1979 from *Senecio oxyodontus*,[2] was assigned the angular triquinane structure **1** on the basis of detailed spectroscopic



1

Scheme I



analysis. The unusual arrangement of the methyl substituents in **1**, which differentiates it from isocomene, silphinene, and pentalenene, has provided the impetus for biogenetic considerations[3] linking senoxydene to botrydial and quadrone. The current widespread interest in naturally occurring polyquinanes[4] prompts us to report at this time an unambigous, fully stereocontrolled synthesis of compound **1** which demonstrates that senoxydene cannot be constituted as originally proposed.

Careful retrosynthetic analysis of the substitution plan in **1** suggested that elaboration of the lower bicyclo[3.3.0]octane moiety, with proper attention to the stereochemical relationship of the secondary methyl group to the angular proton, might well be pursued first. Adoption of this protocol would require that a new cyclopentane annulation scheme be later implemented in a manner that would set the endocyclic double bond and associated methyl group regiospecifically into position.

With these goals in mind, 4,4-dimethylcyclopentenone was treated with 4-butenylmagnesium bromide in the presence of cuprous bromide–dimethyl sulfide complex to give **2** (65%).[5] When heated in a sealed tube at 320 °C for 80 min, the trisubstituted cyclopentanone smoothly entered into intramolecular ene cyclization[6] to provide epimerically pure **3a** (78%). Because the invariant response of **3a** to a host of bases was to produce the less substituted enolate irrespective of conditions, functionalization of the central α-carbonyl site required preliminary conversion to **3c** (62% overall). Subsequent deprotonation with lithium diisopropylamide in tetrahydrofuran at −30 °C and treatment with (*E*)-1-iodo-2-(trimethylsilyl)-2-butene (**4**)[7] led to **5a**. Although significant levels of strain and steric congestion had to be overcome, the primary nature of the leaving group in **4** and careful optimization of the alkylation conditions (−30 °C, warm to 20 °C during 4 h) consistently delivered **5a** in 45% yield. For the usual reasons,[4] retention of cis stereochemistry in the bicyclooctanone was fully expected (Scheme I).

Following removal of the blocking group (reflux, 48 h, 45%), the vinylsilane functionality was converted quantitatively into the epoxide. Without purification, acid-catalyzed isomerization[8] resulted in conversion to diketone **6** (65%). Base-promoted cyclization furnished enone **7** in 82% yield. The structural assign-

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(1) Author to whom inquiries regarding the X-ray analysis should be directed at the Merck address.

(2) Bohlmann, F.; Zdero, C. *Phytochemistry* **1979**, *18*, 1747.

(3) Roberts, J. S. *Terpenoids Steroids* **1981**, *10*, 104.

(4) Paquette, L. A. *Top. Curr. Chem.* **1979**, *79*, 41; **1983**, *119*, in press.

(5) All new compounds exhibited compatible infrared, proton magnetic resonance, and mass spectroscopic data. In addition, the elemental composition of all key intermediates has been substantiated by combustion analysis. Yields refer to isolated chromatographically homogeneous materials.

(6) Beslin, R.; Bloch, R.; Moinet, G.; Conia, J.-M. *Bull. Soc. Chem. Fr.* **1969**, 508.

(7) Iodide **4** was prepared in 59% overall yield by reaction of 2-(trimethylsilyl)-1-buten-3-ol [Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Org. Chem.* **1978**, *43*, 1526] with sulfene [Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195] and S_N2' displacement of mesylate ion with sodium iodide in acetone.

(8) Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, *93*, 2080.

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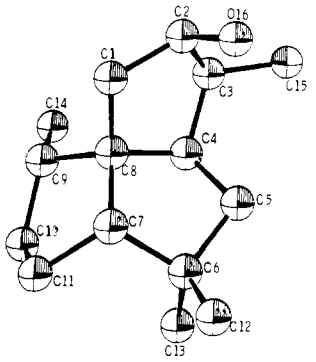
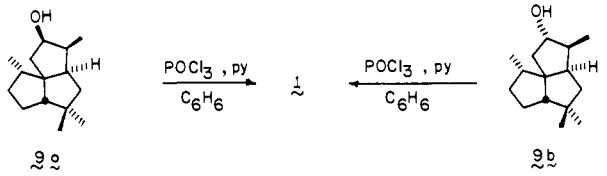


Figure 1. A computer-generated drawing of **9a** derived from the X-ray coordinates. Hydrogens have been omitted and no absolute stereochemistry is implied.

Scheme II



ment to **7** was supported by infrared absorptions at 1710 and 1660 cm^{-1}, a fully consistent ^1H NMR spectrum [($CDCl_3$) δ 2.60 (d, J = 18 Hz, 1 H), 2.40 (d, J = 18 Hz, 1 H), 2.31-1.61 (m, 7 H), 1.72 (d, J = 1.5 Hz, 3 H), 1.19 (m, 1 H), 1.12 (s, 3 H), 0.80 (s, 3 H), 0.71 (d, J = 7.0 Hz, 3 H)], and combustion analysis.

With **7** in hand, our plan called for dissolving metal reduction as a means of saturating the conjugated double bond with a high guarantee that the β hydrogen would enter from the α face to generate the thermodynamically more stable ring juncture. In actuality, the action of lithium in liquid ammonium on **7** gave a single ketone (^{13}C NMR), which was directly reduced with sodium borohydride to obtain pure samples of **9a** (mp 50-52 °C) and **9b** (mp 78-80 °C) after silica gel chromatography (84% combined, Scheme II).

Although the relative configurations of the neighboring hydroxyl and methyl substituents were not yet known, both isomers could be uneventfully dehydrated to **1**. The C_{15} hydrocarbon so obtained was immediately recognized to differ by ^1H NMR from the natural product (Table I).[9]

So that the correctness of the assembly of atoms in the synthetic material could be established, the lower melting saturated alcohol was directly subjected to X-ray analysis.[10] The clear-cut confirmatory definition of this substance as **9a** (Figure 1) suggests that **9b** is likely the α-hydroxy β-methyl derivative. More importantly, the amassed body of knowledge leaves no doubt that senoxydene has been incorrectly formulated. Currently, it is our intention to establish the proper structure of the sesquiterpene by independent synthesis.

Table I. Comparison of the ^1H NMR Spectra of Natural Senoxydene and **1**[a]

natural senoxydene[b]	synthetic **1**[c]
0.84 (d)	0.85 (d)
1.08 (s)	0.93 (s)
1.17 (s)	0.99 (s)
1.60 (ddd)	1.65 (ddd)

[a] $CDCl_3$ solution, methyl signals only. [b] Recorded at 270 MHz. [c] Recorded at 200 MHz.

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by the National Institutes of Health through Grant GM-28468.

Supplementary Material Available: Tables containing the fractional coordinates, temperature parameters, bond distances, and bond angles for **9a** (2 pages). Ordering information is given on any current masthead page.

Asymmetric Induction in the Intramolecular 1,3-Diyl Trapping Reaction. Chirality on the Linking Chain

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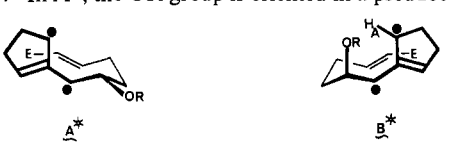
The intramolecular 1,3-diyl trapping reaction has proven to be a very useful process for the construction of the linearly fused tricyclopentanoid ring system, one which is common to a number of natural products.[3] A variety of experiments have served to demonstrate that the stereo- and regiochemical outcome of the reaction is influenced by conformational, stereoelectronic, and steric factors.[4]

One intriguing aspect of the reaction which has received comparitively little attention is that of asymmetric induction. Two reasonable approaches that might be explored in an effort to achieve asymmetric induction include (a) the use of a chiral ester attached to the diylophile π bond and (b) the placement of an asymmetric center on the carbon chain that links the diylophile to the diyl. In both instances, the objective, of course, is to bias the direction associated with the coiling of the linking chain. While the first approach leads to insignificant amounts of asymmetric induction,[5] we are pleased to report that the second provides exceptionally useful results (vide infra).

The plan is illustrated below. Focus attention upon the two cis,anti ring-junction-producing transition-state representations A* and B*. In A*, the OR group is oriented in a pseudoequatorial



A* B*

fashion, while in B*, it is pseudoaxial; in both, the configuration at the carbon bearing the OR units is *S*. On the basis of the results of previous experiments,[6] it can reasonably be argued that the nonbonded interaction between the pseudoaxial OR group and

(9) The authors are indebeted to Professor Bohlmann for making a copy of the senoxydene spectrum available to them. Although only the methyl shifts are summarized in Table I, other spectral differences between the two samples are also clearly apparent.

(10) Suitable crystals of **9a** formed as thick rods from ether at -10 °C. Preliminary diffraction experiments indicated the cell constants to be $a = b$ = 18.082 (3) Å and c = 8.559 (1) Å with space group symmetry $P4_2/n$ (origin at $\bar{1}$). Because crystals of **9a** sublimed at room temperature, the crystal used for data collection was sealed in a thin-walled glass capillary. A total of 2197 unique reflections were measured with a four circle diffractometer and Cu radiation (λ = 1.5418 Å). Of these, 1239 were observed ($I \geq 3\sigma(I)$) and corrected for Lorentz and polarized effects. Application of a multisolution tangent formula approach to phase solution gave an initial model, which was subsequently refined using Fourier methods and full-matrix least-squares analysis. Positions and anisotropic temperature parameters were refined for the non-hydrogen atoms while just the positions for the hydrogens were refined. The function $\sum\omega(|F_o| - |F_c|)^2$ with $\omega = 1/F_o^2$ was minimized to give an unweighted residual index of 0.062. Figure 1 is a perspective drawing of **9a** showing the relative stereochemistry, while Tables II-IV (supplementary material) contain the fractional coordinates, temperature parameters, bond distances, and bond angles. The only short contact is an intermolecular hydrogen bond between 016 and a symmetry related 016 of length 2.81 Å.

(1) Alfred P. Sloan Foundation Fellow, 1980-1984.

(2) UCSB Graduate Student Fellowship awardee.

(3) See, for example, the references in: Greene, A. E.; Luche, M.-J.; Depres, J.-P. *J. Am. Chem. Soc.* **1983**, *105*, 2435.

(4) (a) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* **1981**, *37*, 4371. (b) Little, R. D.; Carroll, G. L. *Tetrahedron Lett.* **1981**, *22*, 4389.

(5) Little, R. D.; Moeller, K. D. *J. Org. Chem.*, in press.

(6) Little, R. D.; Carroll, G. L.; Petersen, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 928.

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