Synthesis of All Stereoisomers of Eudesm-11-en-4-ol. 2. Total Synthesis of Selin-11-en-4α-ol, Intermedeol, Neointermedeol, and Paradisiol. First Total Synthesis of Amiteol

Ronald P. W. Kesselmans, Joannes B. P. A. Wijnberg,* Adriaan J. Minnaard, Robert E. Walinga, and Aede de Groot*

Laboratory of Organic Chemistry, Agricultural University, Dreyenplein 8, 6703 HB Wageningen, The Netherlands

Received May 29, 1991

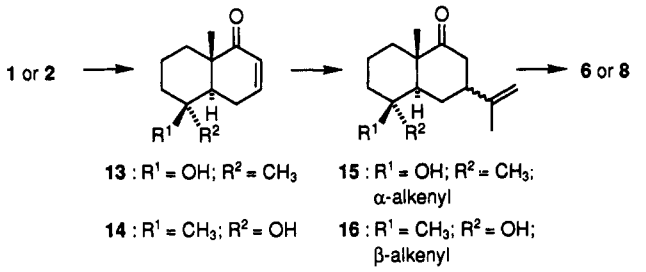
The syntheses of (±)-selin-11-en-4α-ol (**5**), (±)-intermedeol (**6**), (±)-neointermedeol (**7**), (±)-amiteol (**9**), and the four remaining unnatural stereoisomers (±)-paradisiol (**8**), (±)-7-*epi*-amiteol (**10**), (±)-5-*epi*-neointermedeol (**11**), and (±)-5-*epi*-paradisiol (**12**) are described. In addition, the related (±)-evuncifer ether (**25**) has been prepared. The syntheses started from the octahydro-8-hydroxy-4a,8-dimethyl-2(1*H*)-naphthalenones **1–4**. The reaction sequence employed for the synthesis of **5**, **7**, **9**, and **12** involved Wittig reaction, oxidative hydroboration, oxidation, equilibration, and olefination. For the synthesis of **6**, **8**, **10**, and **11** the interim equilibration step was omitted. The oxidative hydroboration was the key step in these syntheses.

In the preceding paper,[1] we have described a method for the synthesis of the trans- and cis-fused hydroxy ketones **1–4** which might be used as key intermediates in the total synthesis of the stereoisomeric eudesmane alcohols **5–12**. Some of these compounds, i.e., intermedeol (**6**),[2] neointermedeol (**7**),[3] and amiteol (**9**)[4] have been found in the defensive secretion of termite soldiers. Selin-11-en-4α-ol (**5**)[5] and also **6**[6] and **7**[7] occur in plants of different sources. Despite their frequent occurrence in nature, the characterization of these compounds is often problematical primarily for lack of clear spectroscopic data. In this paper, we describe the total synthesis of all stereoisomers **5–12** of eudesm-11-en-4-ol[8] starting from the hydroxy ketones **1–4**, with the object of establishing their relative configuration unambiguously. The compilation of the NMR spectroscopic data can be of particular value in the analysis and characterization of this type of eudesmane sesquiterpenes.

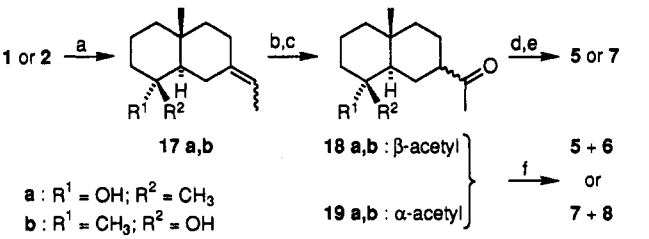
In the synthesis of the trans-fused decalins **5–8** we anticipated that the conversion of the carbonyl group of the hydroxy ketones **1** and **2** into the eudesmanes **6** and **8** with a less favorably orientated 1-methylethenyl substituent could lead to some difficulties. The conformational mobility of the cis-fused decalin structure makes the stereochemical outcome difficult to predict for the eudesmanes **9–12** (Figure 1).

For conformationally fixed trans-fused compounds an elegant solution to the problem of producing an axial 1-methylethenyl group has been reported.[9] This method could not be applied in our approach because the strongly acidic conditions in this reaction led to dehydration of the tertiary alcohol group. Therefore, the introduction of the

Scheme I



Scheme II[a]



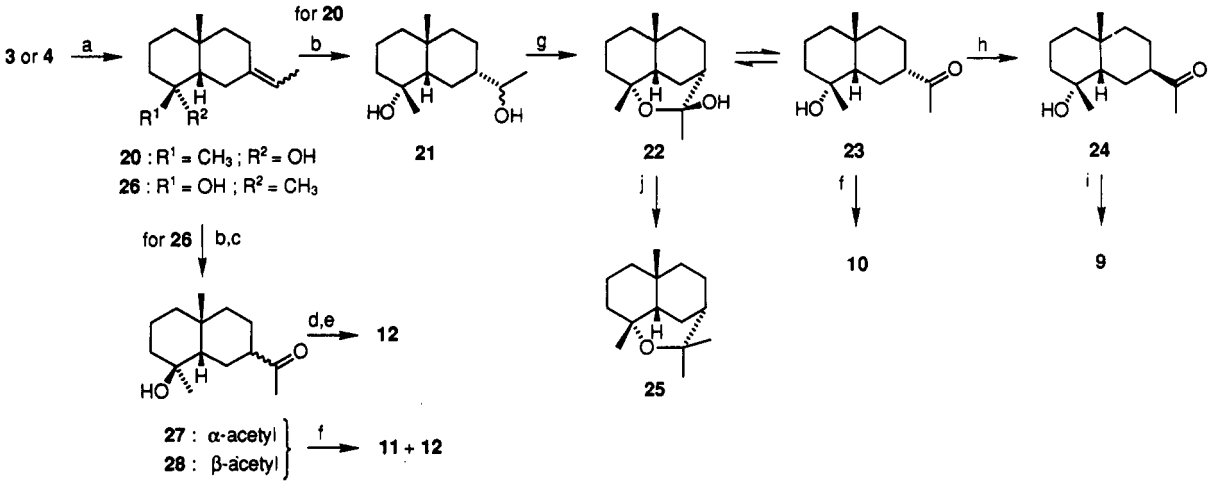
[a] Key: (a) $Ph_3P{=}CHCH_3$, DMSO; (b) $BH_3{\cdot}THF$; H_2O_2, NaOH; (c) PDC, CH_2Cl_2; (d) KOH, CH_3OH; (e) $Ph_3P{=}CH_2$, DMSO; (f) $(CH_3)_3SiCH_2Li$, THF; KH, THF.

axial alkenyl group via a stereoelectronic controlled 1,4-addition of a cuprate reagent to the α,β-unsaturated ketones **13** and **14** was investigated (Scheme I). These compounds were prepared from the corresponding hydroxy ketones via reported methods.[10] Conjugate addition of $Li_2(i\text{-}C_3H_5)_2Cu(I)CN$[11] to **13** gave **15** as a single stereoisomer. Two methods were employed for the conversion of **15** into **8**. A Wolff–Kishner reduction gave **8** in low yield. The other method involved the reduction of the carbonyl group to an alcohol followed by a deoxygenation reaction.[12] The disadvantage of this method is the nonselective reduction of the carbonyl group which gave almost equal amounts of the α- and β-alcohols. The α-alcohol could not be converted into the corresponding xanthate in the deoxygenation reaction, while the application of this reaction

(1) Kesselmans, R. P. W.; Wijnberg, J. B. P. A.; de Groot, Ae.; de Vries, N. K. *J. Org. Chem.* 1991, preceding paper.
(2) Valterova, I.; Krecek, J.; Vrkoc, J. *J. Acta Entomol. Bohemoslov.* 1988, *85*, 241.
(3) Prestwich, G. D.; Collins, M. S. *Biochem. System. Ecol.* 1981, *9*, 83.
(4) Nava, Y.; Prestwich, G. D.; Spanton, S. G. *Tetrahedron Lett.* 1982, *23*, 3047.
(5) Matsou, A.; Ishii, O.; Suzuki, M.; Nakayama, M.; Hayashi, S. *Z. Naturforsch., B* 1982, *37b*, 1636.
(6) San Feliciano, A.; Medarde, M.; Del Rey, B.; Miguel del Corral, J. M.; Barrero, A. F. *Phytochemistry* 1990, *29*, 3207.
(7) Pinder, A. R.; Kerr, S. K. *Ibid.* 1980, *19*, 1871.
(8) This numbering system follows the original eudesmane numbering.
(9) Silvestri, M. G.; Bednarski, P. J.; Kho, E. *J. Org. Chem.* 1985, *50*, 2798.
(10) (a) Grundke, G.; Keese, W.; Rimpler, M. *Chem. Ber.* 1985, *118*, 4288. (b) Sasson, I.; Labovitz, J. *J. Org. Chem.* 1975, *40*, 3670. (c) Liu, H. J.; Wynn, H. *Can. J. Chem.* 1986, *64*, 658.
(11) Ando, M.; Sayama, S.; Takase, K. *J. Org. Chem.* 1985, *50*, 251.
(12) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* 1975, 1574.

0022-3263/91/1956-7237$02.50/0

Scheme III[a]



[a] Key: (a) $Ph_3P{=}CHCH_3$, DMSO; (b) BH_3·THF; H_2O_2, NaOH; (c) PDC, CH_2Cl_2; (d) KOH, CH_3OH; (e) $Ph_3P{=}CH_2$, DMSO; (f) $(CH_3)_3SiCH_2Li$, THF; KH, THF; (g) NDC, pyridine, CH_2Cl_2; (h) *t*-BuOK, DMSO; (i) Zn, CH_2I_2, $TiCl_4$, THF; (j) $BF_3{\cdot}O(C_2H_5)_2$, $(CH_3)_2Li_2Cu(I)CN$, ether.

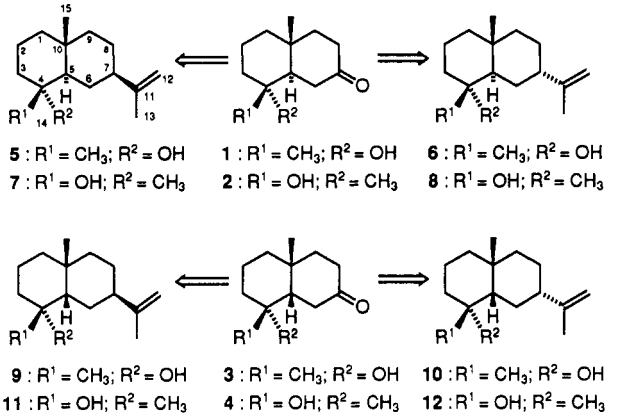


Figure 1.

to the β-alcohol gave **8** in poor yield.

The conversion of **14** into **6** was even less satisfactory. With the unprotected tertiary alcohol group in **14**, the cuprate addition proceeded only when forced reaction conditions were applied and the ketone **16**, with an equatorial 1-methylethenyl group, was isolated as the reaction product. Protection of the tertiary alcohol group in **14** as its TMS ether successively followed by cuprate addition, reduction, deoxygenation, and deprotection finally did give **6**, but again in a low yield.

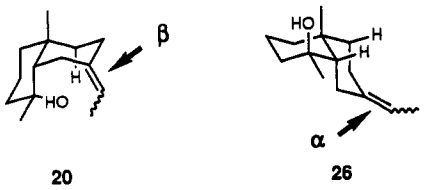
On the other hand, a well-established procedure is available for the introduction of a thermodynamically more stable equatorial 1-methylethenyl substituent starting from the carbonyl group in trans- and cis-fused decalones.[13,14] This synthetic sequence is exemplified in Scheme II and involves the conversion of a carbonyl group into an ethylidene substituent, oxidative hydroboration, oxidation, and a base-catalyzed equilibration, resulting in an equatorially orientated acetyl substituent. A subsequent Wittig olefination then generates the desired 1-methylethenyl group. This reaction sequence was successfully employed in the synthesis of the eudesmane alcohols **5**, **7**, **9**, and **12**. During the synthesis of **5** we noticed that the oxidative hydroboration of the olefin **17a** gave an adduct with an axial substituent at C(7) as the main product, probably as a result of the preferentially equatorial attack of the BH_3 reagent.[15] This selectivity can be used in a straightforward route to the remaining eudesmane alcohols **6**, **8**, **10**, and **11**, as is demonstrated in this paper.

For the synthesis of **5** and **6** the trans-fused hydroxy ketone **1** was the starting material (Scheme II). Treatment of **1** with $Ph_3P{=}CHCH_3$ in DMSO yielded **17a** as a 1:1 mixture of geometric isomers. Oxidative hydroboration (BH_3·THF; NaOH, H_2O_2) of **17a**, directly followed by oxidation with PDC in CH_2Cl_2, gave a 1:2.3 mixture of **18a** and **19a**, respectively.[16] Equilibration of this mixture with KOH in CH_3OH afforded **18a** as the sole product. From these results it was concluded that BH_3 attacks **17a** preferentially from the β side. Pure **5** was obtained upon treatment of **18a** with $Ph_3P{=}CH_2$ in DMSO in an overall yield of 53% starting from **1**. For the preparation of **6**, the original 1:2.3 mixture of **18a** and **19a** was subjected to silyl-Wittig olefination reaction conditions ($(CH_3)_3SiCH_2Li$, THF; KH, THF)[17] to afford a 1:2.3 mixture of **5** and **6**, respectively. It is obvious that during this reaction no epimerization occurs.[18] Although the separation of **5** and **6** was not easy to perform, careful chromatography gave pure **6** in an overall yield of 39% from **1**.

Starting from the hydroxy ketone **2**, the procedure outlined above, i.e., **2** → **17b** → **18b** + **19b** (ratio 1.3:1),[19] followed by equilibration and a Wittig reaction afforded **7** in an overall yield of 58%. Without the interim equilibration step an 1.3:1 mixture of **7** and **8**, respectively, was obtained after the silyl-Wittig reaction. This mixture could be separated, and **8** was isolated in an overall yield of 33% from **2** (Scheme II).

In a similar reaction sequence as applied to the synthesis of **5**–**8**, the *cis*-eudesmane alcohols **9**–**12** could be prepared from the hydroxy ketones **3** and **4**. Treatment of **3** with $Ph_3P{=}CHCH_3$ in DMSO afforded **20** as a 1:1 mixture of geometric isomers. The oxidative hydroboration (BH_3·

(13) Marshall, J. A.; Pike, M. T.; Carroll, R. D. *J. Org. Chem.* **1966**, *31*, 2933.
(14) Rao, P. N. *Ibid.* **1971**, *36*, 2426.
(15) Brown, H. C.; Liotta, R.; Brener, L. *J. Am. Chem. Soc.* **1977**, *99*, 3427.
(16) The oxidative hydroboration of **17a** with the more bulky 9-BBN followed by oxidation with PDC gave a 3:1 mixture of **18a** and **19a**, respectively. This result suggests that the hindrance of the angular methyl group becomes dominant when 9-BBN is used.
(17) Johnson, C. R.; Tait, B. D. *J. Org. Chem.* **1987**, *52*, 281.
(18) Using standard Wittig reaction conditions ($Ph_3P{=}CH_2$, DMSO) epimerization at C(7) was observed.
(19) Probably, the axial hydroxyl group at C(4) hinders the equatorial attack from the β side in the hydroboration of **17b** with BH_3.



20 26

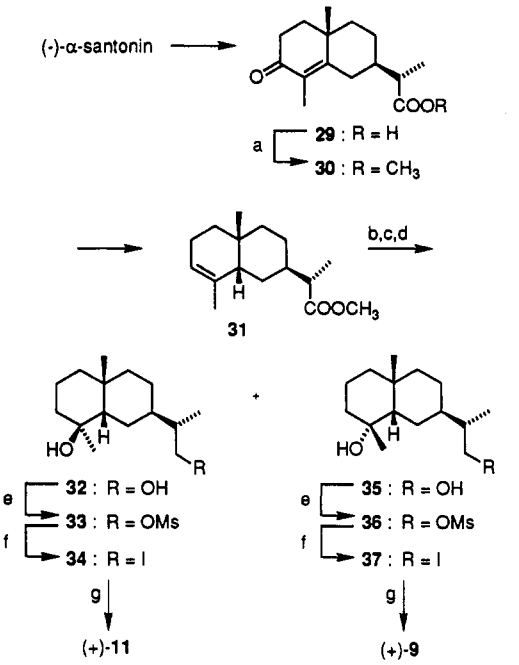
Figure 2.

THF; NaOH, H_2O_2) of the olefinic alcohol **20** provided a diastereomeric 1:1 mixture of only two diols to which structure **21** was assigned (Scheme III). Since we assume that **20** consists in the nonsteroid conformation, just as **3**,[1] one would expect the borane reagent to approach the double bond in **20** from the more open convex face of the molecule. This can explain the selective formation of **21**. The structure of **21** was further confirmed after treatment with NDC and pyridine in CH_2Cl_2,[20] which gave the crystalline lactol **22** in 90% yield. Furthermore, the IR, ^1H NMR, and ^{13}C NMR spectral data of **22** show the presence of the α-acetyl alcohol **23** in about 20%. Thus, in solution the lactol **22** exists in equilibrium with its open form **23**. This observation led us to examine the base-catalyzed equilibration of the lactol **22** in order to prepare a suitable intermediate for the synthesis of **9**. The best result was obtained when **22** was treated with 2 equiv of *t*-BuOK in DMSO at room temperature for a short period (1 min). In this way an easily separable mixture of the β-acetyl alcohol **24** (59%) and **22** (25%) was produced. Longer reaction times gave lower yields of **24**, probably as a result of aldol condensation reactions.[21] Treatment of **24** with zinc powder and CH_2I_2 under the influence of titanium(IV) chloride in dry THF[22] gave (±)-**9** as the sole product in 74% yield (27% overall from **3**).[23] Reaction of **22** with 4 equiv of $Ph_3P{=}CH_2$ in DMSO also afforded (±)-**9**, but now together with its C(7) epimer **10** in isolated yields of 45 and 42%, respectively. Clearly, during this Wittig reaction partial epimerization at the C(7) position of **23** had occurred. On the other hand, after a silyl-Wittig olefination reaction of the lactol **22** no epimerization at all was observed and **10** was produced in an overall yield of 61% starting from **3**.

The lactol **22** is also a highly suitable intermediate for the synthesis of the (±)-evuncifer ether (**25**), the main component of the defensive secretion of *Armitermes evuncifer*.[24] Recently, a method has been reported in which a direct reaction of δ-lactols with modestly nucleophilic organometals in the presence of a Lewis acid provided substituted tetrahydropyrans.[25] The application of a modified version of this method to **22**, using $Li_2(CH_3)_2Cu(I)CN$ in place of dimethylzinc, afforded **25** in 64% yield[26] (39% overall from **3**).

The unnatural cis-fused eudesmane alcohols, **11** and **12**, were prepared from the hydroxy ketone **4** in a similar fashion as described for the synthesis of **9** and **10** starting from **3** (Scheme III). When **4** was subjected to a Wittig reaction with $Ph_3P{=}CHCH_3$ in DMSO the olefinic alcohol **26** was produced as a 3:1 mixture of geometric isomers.

Scheme IV[a]



[a] Key: (a) $(CH_3)_3SiCl$, CH_3OH; (b) Oxone, acetone, 18-crown-6, $NaHCO_3$, H_2O, CH_2Cl_2; (c) $LiAlH_4$, THF; (d) separation; (e) MsCl, pyridine; (f) NaI, acetone; (g) *t*-BuOK, *t*-BuOH.

The oxidative hydroboration of **26**, which is thought to exist predominantly in the steroid conformation,[1] gave a mixture of at least three diols, which without further purification was oxidized with PDC to afford an inseparable mixture of the epimeric acetyl compounds **27** and **28** in a ratio of 1:2.3, respectively. It is obvious that the conformation of the cis-fused compounds **20** and **26** plays an important role in directing the incoming hydroborating reagent. The hydroboration of **20** (nonsteroid) proceeds stereospecifically from the β side. On the other hand, in the hydroboration of **26** (predominantly steroid) the favored attack is from the α side (Figure 2).

The 1:2.3 mixture of **27** and **28** was equilibrated with KOH in CH_3OH to a 19:1 mixture. Treatment of this 19:1 mixture with $Ph_3P{=}CH_2$ in DMSO and recrystallization of the resulting product gave pure **12** in an overall yield of 52% from **4**. The spectroscopic data of **12** were identical with those of a cis-fused eudesmane alcohol synthesized previously.[27] The structure of this latter product has been determined by X-ray crystallography thus supporting the stereochemical assignments of the epimeric acetyl alcohols **27** and **28** (vide supra).

For the preparation of **11**, the original 1:2.3 mixture of **27** and **28** was subjected to silyl-Wittig olefination reaction conditions to afford a mixture of **11** and **12** in high yield. According to GC and ^1H NMR analysis, this mixture consisted of 70% of **11** as the main product and 30% of **12**. Unfortunately, **11** was separated only with difficulty from the minor product **12**. After careful chromatography a sample of 93% pure (±)-**11** could be obtained in a moderate yield of 55%. To prepare pure **11**, we examined a more effective synthesis starting from the commercially available (−)-α-santonin. Via a slightly modified version of a known procedure[28] (−)-α-santonin was converted into the cis-fused olefinic ester **31**, i.e., (−)-α-santonin → **29** →

(20) Cossio, F. P.; Lopez, M. C.; Palomo, C. *Tetrahedron* **1987**, *43*, 3963.
(21) Caine, D. *Org. Prep. Proced. Int.* **1988**, *20*, 1.
(22) Hibino, J.; Okazoe, T.; Takai, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5579.
(23) When **24** was subjected to silyl-Wittig conditions no reaction at all was observed.
(24) Baker, R.; Evans, D. A.; McDowell, P. G. *Tetrahedron Lett.* **1978**, 4073.
(25) Tomooka, K.; Matsuzawa, K.; Suzuki, K.; Tsuchihashi, G. *Ibid.* **1987**, *28*, 6339.
(26) The yield is lowered because of the volatility of **25**.
(27) Baker, R.; Organ, A. J.; Walmsley, S. A.; Webster, M.; Galas, A. M. R. *J. Chem. Res. Miniprint* **1984**, 1401.
(28) (a) Kulkarni, K. S.; Rao, A. S. *Tetrahedron* **1965**, *21*, 1167. (b) Harapanhalli, R. S. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3149. (c) Harapanhalli, R. S. *Ind. J. Chem., Sect. B* **1988**, *27*, 884.

Table I. Selected ^{13}C NMR Data (50 MHz) for the Eudesmane Alcohols 5–12 in $CDCl_3$

		trans-eudesmanes				*cis*-eudesmanes			
signal[a]	C[b]	5	6	7	8	9	10	11	12
CH	5	54.69	49.08	51.84	45.82	47.66	53.03	49.01	51.91
	7	46.19	39.25	46.67	39.13	39.62	45.32	39.31	45.49
CH_3	13	21.00	22.65	20.69	22.59	20.92	21.09	21.29	20.73
	14	22.58	22.21	30.23	29.78	31.23	31.15	30.30	31.20
	15	18.61	18.38	18.66	18.31	29.49	30.50	28.91	30.65

[a] Multiplicities are obtained from DEPT experiment. [b] Assignments are made from COSY and ^1H–^{13}C heteronuclear shift correlation experiments.

30 → **31** (Scheme IV). Epoxidation of **31** with in situ generated dimethyldioxirane[29] and subsequent reduction with $LiAlH_4$ led to a mixture of diols which could be readily separated. The major diol **32**, isolated in 70% yield, was converted into the corresponding iodide **34** via its monomesylate **33**. The iodide **34** could be dehydrohalogenated with *t*-BuOK in refluxing *t*-BuOH to afford the desired optically active unnatural (+)-**11** in an overall yield of 75% from diol **32**. In an analogous fashion, i.e., **35** → **36** → **37** → **9**, the minor diol **35** gave natural (+)-**9** in an overall yield of 58%.

The compilation of the ^{13}C shielding data of the eight stereoisomers **5**–**12** of eudesm-11-en-4-ol can be helpful to the structural identification of similar compounds found in nature (Table I). The resonances attributed to C(15) in **5**–**12** are distinguishing in the determination of the stereochemistry at C(5). In the cis-fused compounds **9**–**12** the C(15) signals have shieldings in the range of 28.9–30.7 ppm, while the corresponding absorptions in the trans-fused compounds **5**–**8** are found at about 18.5 ppm.[30] The shielding data of the C(14) signals in the trans-fused compounds correlate with the stereochemistry at C(4). When C(14) has the β orientation, as in **5** and **6**, the signals appear at about 22.5 ppm. In contrast, the downfield shifts of C(14) at about 30.0 ppm in the spectra of **7** and **8** coincide with the α orientation of this methyl group. Distinction between **5** with an equatorial substituent at C(7) and **6** with an axial substituent at the same carbon can be made by comparison of the CH signals which appear at 54.69 and 46.19 ppm for **5**, and at 49.08 and 39.25 for **6**. Similar differences are observed for **7** and **8**. The distinction between the cis-fused compounds is less obvious. Although significant differences between **9** and **11** on the one hand and between **10** and **12** on the other are observed for the CH signals, no further distinction can be made. However, in combination with their ^1H NMR spectra the differentiation between **9** and **11**, and between **10** and **12**, becomes obvious. The ^1H NMR spectrum of **9** shows a multiplet at 2.64 ppm, while the corresponding signal in **11** appears at 2.26 ppm. The differences of the chemical shifts of the methyl groups at C(4) and C(10) are significant for the distinction between **10** and **12**: 0.40 and 0.05 ppm for **10** and **12**, respectively.

Experimental Section

Melting points were determined on an Olympus HSA melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Philips PU 9706 infrared spectrophotometer, and peak positions are expressed in cm^{-1}. NMR spectra were recorded on a Varian EM-390 at 90 MHz (^1H) and a Bruker 200 E at 200 MHz (^1H) and at 50 MHz (^{13}C). Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (δ 0.0). NMR multiplicities are recorded by use of the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet; br, broad; *J*, coupling constant; Hz, hertz. Mass spectral data were determined on either an AEI MS 902 spectrometer or a Hewlett-Packard 5970B series MSD coupled with a Hewlett-Packard 5890A gas chromatograph with a DB-17 fused silica capillary column, 30 m × 0.25 mm i.d., film thickness 0.25 μm. Elemental analyses were determined on a Carlo Erba elemental analyzer 1106. Gas–liquid chromatography (GC) analyses were carried out on a Varian Vista 6000 gas chromatograph with a flame ionization detector and a DB-17 fused silica capillary column, 30 m × 0.25 mm i.d., film thickness 0.25 μm. Peak areas were integrated electronically with a Spectra-Physics integrator SP 4290. Flash chromatography was performed using Merck silica gel 60 (230–400 mesh).

Solvents were dried and distilled fresh by common practice. For all dry reactions, flasks were dried at 150 °C and flushed with dry nitrogen just before use, and reactions were carried out under an atmosphere of dry nitrogen. Product solutions were dried over anhydrous $MgSO_4$, unless otherwise noted, prior to evaporation of the solvent under reduced pressure by using a rotary evaporator.

Starting Materials. The hydroxy ketones **1**–**4** were prepared as described in the preceding paper.[1]

(1α,4aβ,8aα)-(±)-Decahydro-7-ethylidene-1,4a-dimethyl-1-naphthalenol (17a). To a stirred solution of 75 mL of 0.44 M (dimethylsulfinyl)sodium in dry DMSO at room temperature was added 12.5 g (33.0 mmol) of $Ph_3PCH_2CH_3Br$. After the solution was stirred at room temperature for 30 min, a solution of 2.06 g (10.5 mmol) of hydroxy ketone **1** in 25 mL of dry DMSO was added dropwise. The reaction mixture was stirred at room temperature for 15 h and then poured into 400 mL of water. The aqueous solution was extracted with eight 100-mL portions of EtOAc. The combined organic layers were washed with 200 mL of brine, dried, and evaporated. The remaining residue was flash chromatographed (10:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 1.98 g (91%) of **17a**, which was a mixture of two geometric isomers in a ratio of 1:1, according to GCMS and ^1H NMR analysis: ^1H NMR ($CDCl_3$, 90 MHz) (major peaks) δ 0.96 (s, 3 H), 1.14 (s, 3 H), 5.19 (m, 1 H); mass spectrum (first isomer) *m/e* (relative intensity) 208 (M^+, 23), 190 (39), 175 (32), 121 (38), 93 (28), 81 (30), 67 (30), 43 (100); mass spectrum (second isomer) *m/e* (relative intensity) 208 (M^+, 20), 190 (37), 175 (30), 121 (37), 93 (28), 81 (29), 67 (30), 43 (100).

(2α,4aα,8β,8aβ)-(±)-1-(Decahydro-8-hydroxy-4a,8-dimethyl-2-naphthalenyl)ethanone (18a) and (2α,4aβ,8α,8aα)-(±)-1-(Decahydro-8-hydroxy-4a,8-dimethyl-2-naphthalenyl)ethanone (19a). To a stirred solution of 1.85 g (8.9 mmol) of olefin **17a** in 75 mL of dry THF, cooled to 0 °C, was added dropwise 35 mL (35 mmol) of BH_3·THF (1.0 M in THF). The reaction mixture was stirred at room temperature for 21 h and then heated at reflux for 1 h. The reaction mixture was cooled to 0 °C, after which a mixture of 35 mL of THF and 3.5 mL of water was added dropwise, immediately followed by addition of 21 mL of 3 N NaOH in water and 21 mL of 30% H_2O_2. The reaction mixture was stirred at room temperature for 15 h and then heated at reflux for 1 h. The reaction mixture was allowed to come to room temperature and poured into 200 mL of brine. The two-phase mixture was separated, and the aqueous layer was extracted with four 100-mL portions of CH_2Cl_2. The combined organic layers were dried and evaporated. The resulting oil was dissolved in 250 mL of CH_2Cl_2, and then 10.3 g (27.4 mmol) of PDC was added. The reaction mixture was allowed to stir at room temperature for 20 h and filtered through Celite, and the filter cake was washed with two 100-mL portions of CH_2Cl_2. The solvent was evaporated under reduced pressure, and the resulting residue was flash chromatographed (5:1 petroleum ether (bp 40–60

(29) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.
(30) Caine, D.; Smith, T. L. *Ibid.* **1978**, *43*, 755.

°C)/EtOAc) to give 1.59 g (80%) of a mixture of **18a** and **19a** in a ratio of 1:2.3, respectively, according to GCMS and ^{1}H NMR analysis: ^{1}H NMR ($CDCl_3$, 90 MHz) (major peaks) δ 0.89 (s, 3 H), 1.07 (s, 3 H), 2.16 (s, 3 H), 2.68 (m, $W_{1/2}$ = 12 Hz, 1 H). **18a**: mass spectrum *m/e* (relative intensity) 224 (M^+, 6), 206 (14), 191 (7), 163 (11), 137 (16), 121 (10), 95 (10), 71 (23), 43 (100). **19a**: mass spectrum *m/e* (relative intensity) 206 (M^+ − 18, 33), 191 (30), 163 (11), 147 (13), 121 (7), 81 (19), 71 (18), 43 (100), 41 (20).

(±)-Selin-11-en-4α-ol (5). To a stirred solution of 0.76 g (3.4 mmol) of a 1:2.3 mixture of **18a** and **19a** in 150 mL of absolute CH_3OH was added 2.0 g (36 mmol) of KOH. The reaction mixture was stirred at room temperature for 41 h and then poured into 200 mL of brine. After evaporation of CH_3OH under reduced pressure, the remaining aqueous solution was extracted with five 100-mL portions of EtOAc. The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (4:1–1:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 0.59 g (78%) of pure **18a**: mp 86–87 °C (from diisopropyl ether); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.75–2.60 (m, 15 H), 0.87 (s, 3 H), 1.09 (s, 3 H), 2.13 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.41 (q), 19.94 (t), 22.63 (q), 22.80 (t), 23.50 (t), 28.23 (q), 34.39 (s), 40.78 (t), 43.27 (t), 43.72 (t), 52.19 (d), 53.96 (d), 71.99 (s), 212.08 (s); calcd for $C_{14}H_{24}O_2$ (M^+) *m/e* 224.1776, found 224.1773. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.66; H, 10.88. The procedure described for the synthesis of **17a** was employed by using 50 mL of 0.26 M (dimethylsulfinyl)sodium in dry DMSO, 4.64 g (13.0 mmol) of Ph_3PCH_3Br, and 0.59 g (2.6 mmol) of **18a** in 25 mL of dry DMSO. After stirring at 50 °C for 7 h, the workup and flash chromatography (25:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 0.55 g (94%) of **5**: mp 61–62 °C (from diisopropyl ether); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.75–2.00 (m, 15 H), 0.83 (s, 3 H), 1.06 (s, 3 H), 1.68 (br s, 3 H), 4.65 (br s, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.61 (q), 20.03 (t), 21.00 (q), 22.58 (q), 25.89 (t), 26.74 (t), 34.49 (s), 40.96 (t), 43.23 (t), 44.55 (t), 46.19 (d), 54.69 (d), 72.10 (s), 108.06 (t), 150.49 (s); mass spectrum *m/e* (relative intensity) 222 (M^+, 31), 204 (100), 189 (43), 137 (54), 135 (85), 109 (49), 81 (64), 71 (54), 43 (50); calcd for $C_{15}H_{26}O$ (M^+) *m/e* 222.1984, found 222.1984. Anal. Calcd for $C_{15}H_{26}O$: C, 81.08; H, 11.78. Found: C, 80.71; H, 11.72. Our synthetic (±)-**5** exhibited spectra identical with those of (−)-selin-11-en-4α-ol.[5]

(±)-Intermedeol (6). To a stirred solution of 10 mL of 0.5 M $(CH_3)_3SiCH_2Li$ in 1:1 pentane/THF, cooled to −78 °C, was added dropwise a solution of 0.061 g (0.27 mmol) of a 1:2.3 mixture of **18a** and **19a** in 15 mL of dry THF. When the addition was complete, the reaction mixture was allowed to stir for 30 min at −78 °C. The excess $(CH_3)_3SiCH_2Li$ was then quenched by the careful addition of saturated aqueous NH_4Cl. After addition of 25 mL of water, the two-phase mixture was separated, and the aqueous layer was extracted with three 20-mL portions of EtOAc. The combined organic layers were washed with brine, dried, and evaporated. The remaining residue was taken up in 15 mL of dry THF and added dropwise to a suspension of 0.090 g (2.25 mmol) KH in 10 mL of dry THF. The reaction mixture was stirred at room temperature for 30 min and then diluted with 25 mL of water. The two-phase mixture was separated, and the aqueous layer was extracted with three 20-mL portions of EtOAc. The combined organic layers were washed with brine, dried, and evaporated. The remaining mixture was flash chromatographed (20:1 petroleum ether (bp 40–60 °C)/EtOAc) to give, in order of elution, 0.032 g (53%) of pure **6** and 0.028 g (46%) of a 2:1 mixture of **5** and **6**, respectively.

6: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80–1.89 (m, 13 H), 0.90 (s, 3 H), 1.06 (s, 3 H), 1.72 (br s, 3 H), 2.03 (m, 1 H), 2.40 (m, 1 H), 4.84 (br s, 1 H), 4.88 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.38 (q), 20.06 (t), 22.21 (q), 22.65 (q), 22.65 (t), 23.40 (t), 35.21 (s), 39.25 (d), 40.24 (t), 41.25 (t), 43.42 (t), 49.08 (d), 72.01 (s), 110.72 (t) 146.61 (s); mass spectrum *m/e* (relative intensity) 222 (M^+, 1), 207 (13), 204 (77), 189 (70), 174 (13), 167 (33), 161 (100), 147 (23), 133 (29), 122 (53), 105 (27); calcd for $C_{15}H_{26}O$ (M^+) *m/e* 222.1984, found 222.1984. Our synthetic (±)-**6** exhibited spectra identical with those of (+)-intermedeol.[6]

(1α,4aα,8aβ)-(±)-Decahydro-7-ethylidene-1,4a-dimethyl-1-naphthalenol (17b). The olefin **17b** was prepared in 86% yield from the hydroxy ketone **2** (3.00 g, 15.3 mmol) as described for the synthesis of **17a**. According to GCMS and ^{1}H NMR analysis, **17b** was a mixture of two geometric isomers in a ratio of 7:3: ^{1}H NMR ($CDCl_3$, 90 MHz) (major peaks) δ 1.11 (s, 3 H), 1.19 (s, 3 H), 5.18 (m, 1 H); mass spectrum (major isomer) *m/e* (relative intensity) 208 (M^+, 1.5), 190 (60), 175 (51), 161 (21), 147 (17), 134 (17), 119 (35), 108 (24), 93 (26), 67 (27), 43 (100); mass spectrum (minor isomer) *m/e* (relative intensity) 208 (M^+, 2.1), 190 (53), 175 (46), 161 (20), 147 (16), 134 (16), 119 (32), 108 (23), 93 (24), 67 (28), 43 (100).

(2α,4aα,8aα,8aβ)-(±)-1-(Decahydro-8-hydroxy-4a,8-dimethyl-2-naphthalenyl)ethanone (18b) and (2α,4aβ,8β,8aα)-(±)-1-(Decahydro-8-hydroxy-4a,8-dimethyl-2-naphthalenyl)ethanone (19b). An inseparable mixture of **18b** and **19b** was prepared in 90% yield from the olefin **16** (2.62 g, 12.6 mmol) as described for the oxidative hydroboration and subsequent oxidation of **17a**. According to GCMS and ^{1}H NMR analysis, the ratio of **18b** and **19b** was 1.3:1, respectively: ^{1}H NMR ($CDCl_3$, 90 MHz) (major peaks) δ 1.09 (s, 3 H), 1.18, 1.26 (s, 3 H), 2.20 (s, 3 H). **18b**: mass spectrum *m/e* (relative intensity) 224 (M^+, 0.1), 209 (9), 206 (26), 191 (15), 181 (2), 163 (9), 147 (9), 71 (20), 43 (100). **19b**: mass spectrum *m/e* (relative intensity) 224 (M^+, 4), 209 (18), 206 (7), 191 (6), 181 (8), 163 (10), 137 (11), 71 (21), 43 (100).

(±)-Neointermedeol (7). A sample of the 1.3:1 mixture of alcohol **18b** and **19b** (2.00 g, 8.93 mmol) was equilibrated and treated with $Ph_3P{=}CH_2$ as described for the synthesis of **5** to give 1.49 g (75%) of **7**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.95–2.05 (m, 15 H), 1.03 (s, 3 H), 1.12 (s, 3 H), 1.71 (br s, 3 H), 4.66 (m, 1 H), 4.69 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.03 (t), 18.66 (q), 20.69 (q), 25.76 (t), 26.81 (t), 30.23 (q), 33.66 (s), 41.24 (t), 41.56 (t), 43.85 (t), 46.67 (d), 51.84 (d), 71.92 (s), 108.31 (t), 150.75 (s); mass spectrum *m/e* (relative intensity) 222 (M^+, 16), 207 (82), 204 (100), 188 (54), 171 (29), 145 (61), 105 (91), 81 (51), 71 (41), 43 (49); calcd for $C_{15}H_{26}O$ (M^+) *m/e* 222.1984, found 222.1989. Anal. Calcd for $C_{15}H_{26}O$: C, 81.01; H, 11.78. Found: C, 80.76; H, 11.82. Our synthetic (±)-**7** exhibited spectra identical with those of (+)-neointermedeol.[3]

(±)-Paradisiol (8). A sample of the 1.3:1 mixture of **18b** and **19b** (0.072 g, 0.32 mmol) was treated with $(CH_3)_3SiCH_2Li$ and KH as described for the synthesis of **6**. The workup and flash chromatography (20:1 petroleum ether (bp 40–60 °C)/EtOAc) gave, in order of elution, 0.036 g (53%) of **7** and 0.030 g (42%) of **8**.

8: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80–2.00 (m, 15 H), 1.06 (s, 3 H), 1.13 (s, 3 H), 1.71 (br s, 3 H), 4.78 (br s, 1 H), 4.88 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.81 (t), 18.31 (q), 22.38 (t), 22.59 (q), 23.13 (t), 29.78 (q), 34.14 (s) 39.13 (d), 39.38 (t), 41.01 (t), 41.61 (t), 45.82 (d), 71.83 (s), 110.37 (t), 146.90 (s); mass spectrum *m/e* (relative intensity) 222 (M^+, 8), 207 (14), 204 (26), 189 (20), 161 (23), 135 (16), 123 (21), 109 (23), 81 (47), 43 (100); calcd for $C_{15}H_{26}O$ (M^+) *m/e* 222.1984, found 222.1986. Our synthetic (±)-**8** exhibited spectra identical with those of (+)-paradisiol.[6]

(1a,4aβ,8aβ)-(±)-Decahydro-7-ethylidene-1,4a-dimethyl-1-naphthalenol (20). The olefin **20** was prepared in 86% yield from the hydroxy ketone **3** (6.00 g, 30.6 mmol) as described for the synthesis of **17a**. According to GCMS and ^{1}H NMR analysis, **20** was a mixture of two geometric isomers in a ratio of 1:1: ^{1}H NMR ($CDCl_3$, 90 MHz) (major peaks) δ 1.03 (s, 3 H), 1.20, 1.23 (s, s, 1:1 ratio, 3 H), 5.28 (m, 1 H); mass spectrum (first isomer) *m/e* (relative intensity) 208 (M^+, 0.4), 193 (7), 190 (85), 175 (61), 161 (35), 147 (26), 133 (34), 119 (60), 93 (50), 43 (100); mass spectrum (second isomer) *m/e* (relative intensity) 208 (M^+, 0.4), 193 (7), 190 (82), 175 (60), 161 (35), 147 (25), 133 (35), 119 (61), 93 (51), 43 (100).

(2α,4aβ,8α,8aβ)-(±)-1-(Decahydro-8-hydroxy-4a,8-dimethyl-2-naphthalenyl)ethanol (21). The diol **21** was prepared in 79% yield from **20** (5.49 g, 24.3 mmol) as described for the oxidative hydroboration of **17a**. According to GCMS and ^{1}H NMR analysis, **21** was a 1:1 mixture of two diastereoisomers. Pure samples of the two diastereoisomers were obtained after flash chromatography (2:1 petroleum ether (bp 40–60 °C)/EtOAc).

21 (first diastereoisomer): mp 143–144 °C (from diisopropyl ether); IR ($CHCl_3$) 3670, 3600, 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.73–1.89 (m, 16 H), 0.98 (s, 3 H), 1.15 (d, *J* = 6 Hz, 3 H), 1.39 (s, 3 H), 3.56 (m, $W_{1/2}$ = 16 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.04 (t), 20.37 (q), 23.12 (t), 26.00 (t), 29.13 (t), 30.29 (q), 31.03 (q), 33.97 (s), 34.98 (t), 42.35 (t), 44.80 (d), 52.51 (d),

71.81 (d), 72.71 (s); mass spectrum m/e (relative intensity) 190 ($M^+ - 36$, 27), 175 (12), 161 (13), 150 (15), 123 (43), 121 (26), 95 (29), 81 (45), 71 (37), 67 (32), 43 (100).

21 (second diastereoisomer): mp 147–149 °C (from diisopropyl ether); IR ($CHCl_3$) 3670, 3600, 3400 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.73–1.89 (m, 16 H), 0.98 (s, 3 H), 1.14 (d, J = 6 Hz, 3 H), 1.39 (s, 3 H), 3.56 (m, $W_{1/2}$ = 16 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.18 (t), 20.48 (q), 23.28 (t), 26.12 (t), 29.28 (t), 30.44 (q), 31.16 (q), 34.11 (s), 35.12 (t), 42.51 (t), 44.94 (d), 52.65 (d), 71.92 (d), 72.84 (s); mass spectrum m/e (relative intensity) 190 ($M^+ - 36$, 27), 175 (16), 161 (22), 150 (21), 133 (17), 123 (48), 121 (34), 95 (27), 81 (58), 71 (46), 67 (41), 43 (100).

(±)-(3α,4aβ,5α,8aα)-Octahydro-2-hydroxy-2,5,8a-trimethyl-3,5-ethano-2*H*-1-benzopyran (22). To a stirred solution of 4.21 g (18.6 mmol) of diol **21** in 150 mL of CH_2Cl_2 was added 11.6 g (24 mmol) of NDC and 20.8 mL (240 mmol) of pyridine. The reaction mixture was stirred at room temperature for 70 min, after which time the mixture was filtered through Celite. The filter cake was washed with two 100-mL portions of CH_2Cl_2. The combined organic layers were washed successively with 75 mL of 10% aqueous HCl and 100 mL of a saturated aqueous $NaHCO_3$, dried, and evaporated. The remaining residue was flash chromatographed (10:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 3.78 g (90%) of **22**: mp 101–102 °C (from diisopropyl ether): mass spectrum m/e (relative intensity) 224 (M^+, 2), 209 (21), 206 (15), 191 (11), 164 (34), 149 (35), 109 (100); calcd for $C_{14}H_{24}O_2$ (M^+) m/e 224.1776, found 224.1778. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.91; H, 11.06. The IR, ^1H NMR, and ^{13}C NMR spectra of **22** revealed the presence of **23** in about 20%.

22: IR (CCl_4) 3600 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.68–2.37 (m, 15 H), 0.93 (s, 3 H), 1.32 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.52 (t), 21.11 (t), 24.84 (t), 28.23 (t), 28.77 (q), 29.17 (q), 29.74 (q), 32.42 (s) 34.54 (d), 40.55 (t), 41.21 (t), 42.78 (d), 73.91 (s), 99.26 (s).

23: IR (CCl_4) 1710 cm^{-1}; ^1H NMR (main peaks) ($CDCl_3$, 200 MHz) δ 0.97 (s), 1.37 (s), 2.09 (s); ^{13}C NMR (main peaks) ($CDCl_3$, 50 MHz) δ 20.02 (t), 23.91 (t), 25.64 (t), 30.29 (q) 31.21 (q), 33.84 (s), 35.41 (t), 41.51 (t), 51.32 (d), 52.10 (d), 72.67 (s), 212.51 (s).

(±)-7-*epi*-Amiteol (10). This compound was prepared from the lactol **22** (0.046 g, 0.21 mmol) as described for the synthesis of **6**. The workup and flash chromatography (20:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded 0.045 g (99%) of **10**: mp 112–113 °C (from diisopropyl ether); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.73–2.03 (m, 15 H), 0.99 (s, 3 H), 1.39 (s, 3 H), 1.69 (br s, 3 H), 4.65 (br s, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.26 (t), 21.09 (q), 27.18 (t), 29.40 (t), 29.40 (t), 30.50 (q), 31.15 (q), 33.99 (s), 35.25 (t), 42.96 (t), 45.32 (d), 53.03 (d), 72.81 (s), 108.02 (t), 150.82 (s); mass spectrum m/e (relative intensity) 222 (M^+, 15), 207 (9), 204 (96), 189 (51), 161 (47), 137 (71), 135 (62), 109 (60), 95 (60), 81 (100); calcd for $C_{15}H_{26}O$ (M^+) m/e 222.1984, found 222.1986.

(2α,4aα,8β,8aα)-(±)-1-(Decahydro-8-hydroxy-4a,8-dimethyl-2-naphthalenyl)ethanone (24). To a stirred solution of 0.224 g (2.00 mmol) of *t*-BuOK in 5 mL of dry DMSO was added at once a solution of 0.203 g (0.91 mmol) of **22** in 5 mL of dry DMSO. The reaction mixture was stirred at room temperature for 1 min and then quenched by the addition of 0.13 mL of AcOH. The reaction mixture was poured into 50 mL of water. The aqueous layer was extracted with eight 15-mL portions of EtOAc. The combined organic layers were washed with brine, dried, and evaporated. The remaining residue was flash chromatographed (10:1 petroleum ether (bp 40–60 °C)/EtOAc) to give, in order of elution, 0.051 g (25%) **22** and 0.119 g (59%) of **24**.

24: mp 110–111 °C (from diisopropyl ether); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.85–2.20 (m, 14 H), 0.85 (s, 3 H), 1.16 (s, 3 H), 2.04 (s, 3 H), 3.16 (dddd, J = 4, 4, 13, 13 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.28 (t), 23.04 (t), 23.67 (t), 28.12 (q), 29.09 (q), 31.16 (q), 31.61 (t), 32.56 (s), 41.46 (t), 42.51 (t), 46.46 (d), 46.86 (d), 73.27 (s), 213.79 (s); mass spectrum m/e (relative intensity) 224 (M^+, 8), 209 (4), 206 (82), 191 (19), 163 (31), 148 (5), 137 (24), 121 (16), 109 (40), 95 (20), 81 (32), 71 (40), 43 (100); calcd for $C_{14}H_{24}O_2$ (M^+) m/e 224.1776, found 224.1771.

(±)-Amiteol (9). A solution of 1.57 mL (1.57 mmol) of titanium(IV) chloride (1.0 M in THF) was added dropwise to a mixture of zinc dust (0.96 g, 14.7 mmol) and CH_2I_2 (0.64 mL, 7.95 mmol) in 20 mL of dry THF (argon atmosphere) at 0 °C. The resulting mixture was stirred at room temperature for 30 min, and then a solution of 0.086 g (0.38 mmol) of **24** in 5 mL of dry THF was added dropwise. The reaction mixture was stirred at room temperature for 3.5 h, heated at reflux for 1 h, and then allowed to come to room temperature. Stirring was continued for an additional 17 h, after which time the reaction mixture was diluted with 50 mL of 5% aqueous HCl. The two-phase mixture was separated, and the aqueous layer was extracted with three 25-mL portions of EtOAc. The combined organic layers were washed with brine, dried, and evaporated. The remaining residue was flash chromatographed (20:1 petroleum ether (bp 40–60 °C)/EtOAc) to afford 0.062 g (74%) of **9**: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.94 (s, 3 H), 0.96–2.09 (m, 14 H), 1.22 (s, 3 H), 1.72 (br s, 3 H), 2.64 (ddddd, J = 13, 13, 3, 3, 1 Hz, 1 H), 4.66 (br s, 1 H), 4.68 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.39 (t), 20.92 (q), 26.50 (t), 26.60 (t), 29.49 (q), 31.23 (q), 32.47 (t), 32.79 (s), 39.62 (d), 41.76 (t), 42.57 (t), 47.66 (d), 73.46 (s), 107.56 (t), 151.75 (s); mass spectrum m/e (relative intensity) 204 ($M^+ - 18$, 65), 179 (27), 175 (8), 161 (26), 147 (28), 133 (14), 121 (29), 109 (100), 97 (25); calcd for $C_{15}H_{26}O$ ($M^+ - 18$) m/e 204.1878, found 204.1874. Our synthetic (±)-**9** exhibited spectra identical with those of (+)-amiteol.[4]

(±)-Evuncifer Ether (25). To a stirred solution of 8.3 mL (13.28 mmol) of CH_3Li (1.6 M in ether), cooled to 0 °C, was added 0.630 g (7 mmol) of CuCN. The mixture was allowed to stir at 0 °C for 1 h, after which time it was cooled to −78 °C. To a solution of 0.152 g (0.68 mmol) of lactol **22** in 25 mL of dry ether was added 0.410 mL (3.3 mmol) of freshly distillated boron trifluoride etherate. This mixture was allowed to stand at room temperature for 2 min, and then added at once to the stirred cuprate mixture at −78 °C. The reaction mixture was allowed to stir for 3 min, and then quenched with saturated aqueous NH_4Cl. After addition of 50 mL of water, the two-phase mixture was separated, and the aqueous layer was extracted with two 25-mL portions of EtOAc. The combined organic layers were washed with brine, dried, and evaporated. The remaining residue was flash chromatographed (5:1 pentane/CH_2Cl_2) to give 0.096 g (64%)[26] of **25**: ^1H NMR ($CDCl_3$, 200 MHz) δ 0.65–1.16 (m, 8 H), 1.00 (s, 3 H), 1.23–1.60 (m, 2 H), 1.23 (s, 3 H), 1.28 (s, 3 H), 1.33 (s, 3 H), 1.74–1.95 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.68 (t), 22.16 (t), 25.25 (t), 29.07 (q), 29.07 (q), 29.33 (t), 29.67 (q), 31.02 (q), 32.62 (s), 34.84 (d), 41.05 (t), 42.21 (t), 42.83 (d), 72.88 (s), 74.58 (s); mass spectrum m/e (relative intensity) 222 (M^+, 0.3), 207 (100), 189 (28), 164 (7), 149 (27), 133 (11), 123 (13), 109 (80), 93 (18), 81 (23), 43 (60); calcd for $C_{15}H_{26}O$ (M^+) m/e 222.1984, found 222.1996. Our synthetic (±)-**25** exhibited spectra identical with those of (−)-evuncifer ether.[24]

(1α,4aα,8aα)-(±)-Decahydro-7-ethylidene-1,4a-dimethyl-1-naphthalenol (26). The olefin **26** was prepared in 88% yield from the hydroxy ketone **4** (1.59 g, 8.1 mmol) as described for the synthesis of **17a**. According to GCMS and ^1H NMR analysis, **26** was a 3:1 mixture of two geometric isomers: ^1H NMR ($CDCl_3$, 90 MHz) (major peaks) δ 1.19 (s, 6 H), 5.14 (m, 1 H); mass spectrum (major isomer) m/e (relative intensity) 208 (M^+, 4), 190 (31), 175 (15), 161 (13), 150 (8), 133 (11), 121 (42), 107 (14), 93 (29), 81 (31), 43 (100); mass spectrum (minor isomer) m/e (relative intensity) 208 (M^+, 6), 190 (31), 175 (19), 161 (6), 150 (9), 133 (6), 121 (28), 107 (19), 93 (25), 79 (31), 43 (100).

(2α,4aβ,8β,8aβ)-(±)-1-(Decahydro-8-hydroxy-4a,8-dimethyl-2-naphthalenyl)ethanone (27) and (2α,4aα,8α,8aα)-(±)-1-(Decahydro-8-hydroxy-4a,8-dimethyl-2-naphthalenyl)ethanone (28). An inseparable mixture of **27** and **28** was prepared in 87% yield from the olefin **26** (1.39 g, 6.8 mmol) as described for the oxidative hydroboration and subsequent oxidation of **17a**. According to GCMS and ^1H NMR analysis, the ratio of **27** and **28** was 1:2.3, respectively: ^1H NMR ($CDCl_3$, 90 MHz) (major peaks) δ 1.18 (s, 3 H), 1.24 (s, 3 H), 2.16 (s, 3 H). **27**: mass spectrum m/e (relative intensity) 224 (M^+, 1.4), 209 (1.6), 206 (22), 191 (11), 163 (9), 137 (13), 121 (9), 95 (11), 81 (13), 71 (25), 43 (100). **28**: mass spectrum m/e (relative intensity) 209 ($M^+ - 15$, 14), 206 (8), 167 (6), 163 (7), 149 (6), 139 (8), 121 (8), 95 (12), 81 (12), 71 (24), 43 (100).

(±)-5-*epi*-Paradisiol (12). This compound was prepared from the 1:2.3 mixture of **27** and **28** as described for the synthesis of **5**. After equilibration a 19:1 mixture (1.24 g) of **27** and **28**, respectively, was obtained. Treatment of this 19:1 mixture with $Ph_3P{=}CH_2$ gave, after chromatography and recrystallization from

diisopropyl ether, 0.897 g (68%) of **12**: mp 83–84 °C (lit.[27] mp 77 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80–2.00 (m, 15 H), 1.12 (s, 3 H), 1.17 (s, 3 H), 1.69 (br s, 3 H), 4.65 (br s, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.21 (t), 20.73 (q), 26.60 (t), 29.66 (t), 30.65 (q), 31.20 (q), 31.20 (t), 33.04 (s), 34.17 (t), 42.73 (t), 45.49 (d), 51.91 (d), 74.01 (s), 107.92 (t), 150.59 (s); mass spectrum *m/e* (relative intensity) 222 (M^+, 5), 204 (32), 189 (19), 161 (30), 135 (43), 121 (25), 109 (34), 81 (65), 43 (100); calcd for $C_{15}H_{26}O$ (M^+) *m/e* 222.1984, found 222.1986. Anal. Calcd for $C_{15}H_{26}O$: C, 81.01; H, 11.78. Found: C, 80.85; H, 11.81. Our synthetic (±)-**12** exhibited spectra identical with those of synthetic (-)-**12**.[27]

(±)-5-*epi*-Neointermedeol (11). A sample of the 1:2.3 mixture of **27** and **28** (0.061 g, 0.27 mmol) was treated with $(CH_3)_3SiCH_2Li$ and KH as described for the synthesis of **6**. The workup and flash chromatography (20:1 petroleum ether (bp 40–60 °C)/EtOAc) gave, in order of elution, 0.011 g (18%) of **12**, 0.009 g (15%) of a 2:1 mixture of **11** and **12**, respectively, and 0.033 g (55%) of **11** with a purity of 93% according to GC analysis. The spectroscopic data of this (±)-**11** were identical with those of (+)-**11** (vide infra).

[2*R*-[2α(*S),4aα,8aα]]-1,2,3,4,4a,5,6,8a-Octahydro-α,4a,8-trimethyl-2-naphthaleneacetic Acid, Methyl Ester (31).** The keto acid **29** (5.16 g, 20.7 mmol), prepared from commercially available (-)-α-santonin as described,[28a] was dissolved in 400 mL of CH_3OH and $(CH_3)_3SiCl$ (6.0 mL, 47 mmol) was added. The mixture was stirred at room temperature for 46 h, and then diluted with 250 mL of saturated aqueous $NaHCO_3$. After removal of CH_3OH under reduced pressure, the remaining aqueous solution was extracted with three 150-mL portions of EtOAc. The combined organic layers were dried, and evaporated. The resulting residue was flash chromatographed (4:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 4.68 g (86%) of keto ester **30**. The spectroscopic data of **30** were identical with those in the literature.[28b] A sample of **30** (2.38 g, 9.02 mmol) was converted into the cis-fused olefinic ester **31** in 79% yield as described.[28c]

[2*R*-[2α(*S),4aα,8α,8aα)]]-2-(Decahydro-8-hydroxy-α,4a,8-trimethyl-2-naphthalenyl)ethanol (32) and [2*R*-[2aα(*S**),4aα,8β,8aα)]]-2-(Decahydro-8-hydroxy-α,4a,8-trimethyl-2-naphthalenyl)ethanol (35).** To a stirred solution of 0.935 g (3.74 mmol) of ester **31** in 50 mL of CH_2Cl_2 were added subsequently 50 mL of acetone, 0.081 g (0.31 mmol) of 18-crown-6, and a solution of 1.42 g (16.9 mmol) of $NaHCO_3$ in 50 mL of water. The two-phase mixture was cooled to 0 °C, and then a solution of 2.88 g (4.68 mmol) of oxone in 16 mL of water was added dropwise. The reaction mixture was allowed to stir at 0 °C for 3.5 h, after which time 50 mL of saturated aqueous $Na_2S_2O_3$ and 100 mL of saturated aqueous $NaHCO_3$ were added. The two-phase mixture was separated, and the aqueous layer was extracted with five 50-mL portions of CH_2Cl_2. The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (20:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 0.760 g (76%) of a 1:4 mixture of two epoxides, according to GCMS analysis: mass spectrum (major compound) *m/e* (relative intensity) 266 (M^+, 18), 251 (81), 178 (33), 163 (29), 135 (24), 121 (26), 107 (40), 88 (38), 55 (50), 43 (100); mass spectrum (minor compound) *m/e* (relative intensity) 266 (M^+, 26), 251 (89), 248 (5), 178 (38), 161 (38), 149 (44), 135 (28), 125 (36), 112 (42), 88 (64), 55 (63), 43 (100). To a solution of this epoxide mixture in 50 mL of dry THF was added 0.430 g (11.3 mmol) of $LiAlH_4$. The reaction mixture was heated at reflux for 20 h and, after cooling to 0 °C, quenched with saturated aqueous Na_2SO_4. After addition of 100 mL of water, the reaction mixture was extracted with five 50-mL portion of EtOAc. The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (2:1–1:1 petroleum ether (bp 40–60 °C)/EtOAc) to give, in order of elution, 0.139 g (20%) of **35** and 0.481 g (70%) of **32**. Physical and spectroscopic data of **32** and **35** are shown below.

32: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.91 (d, *J* = 6 Hz, 3 H), 1.00–2.20 (m, 17 H), 1.03 (s, 3 H), 1.20 (s, 3 H), 3.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz)[31] δ 14.67 (q), 19.22 (t), 23.60 (t) 26.05 (t), 29.05 (q), 30.44 (q), 33.65 (s), 34.27 (t), 34.27 (d), 36.53 (t)*, 37.67 (d)*, 39.84 (t)*, 49.17 (d), 65.89 (t), 74.14 (s); mass spectrum *m/e* (relative intensity) 225 (M^+ - 15, 3), 222 (27), 207 (41), 204 (19), 189 (25), 163 (85), 137 (40), 121 (28), 109 (72), 81 (100); calcd for $C_{14}H_{25}O_2$ (M^+ - 15) *m/e* 225.1854, found 225.1845. Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.94; H, 11.74. Found: C, 74.92; H, 11.82.

35: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.65–2.40 (m, 17 H), 0.86 (d, *J* = 7 Hz, 3 H), 0.90 (s, 3 H), 1.21 (s, 3 H), 3.53 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 12.83 (q), 17.20 (t), 22.91 (t), 26.07 (t), 29.26 (q), 29.41 (s), 30.95 (q), 32.18 (t), 32.78 (d), 40.94 (d), 41.51 (t), 42.10 (t), 47.54 (d), 65.99 (t), 73.29 (s); mass spectrum *m/e* (relative intensity) 222 (M^+ - 18, 17), 207 (27), 204 (15), 189 (16), 163 (81), 137 (30), 121 (26), 109 (100), 81 (49); calcd for $C_{15}H_{26}O$ (M^+ - 18) *m/e* 222.1983, found 222.1993.

[7*R*-[1α,4aα,7α(*S),8aα)]]-Decahydro-1-hydroxy-1,4a-dimethyl-7-[1-methyl-2-[(methylsulfonyl)oxy]ethyl]-naphthalene (33).** To a stirred solution of 0.412 g (1.72 mmol) of diol **32** in 20 mL pyridine was added 0.444 g (3.88 mmol) of MsCl. The reaction mixture was stirred at 40 °C for 40 min and then concentrated under reduced pressure. The resulting residue was taken up in 50 mL of EtOAc and washed successively with 25 mL of 10% aqueous H_2SO_4, 50 mL of saturated aqueous $NaHCO_3$, and brine. The organic layer was dried and evaporated. The crude product was flash chromatographed (3:1–2:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 0.474 g (87%) of **33**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.90–1.90 (m, 16 H), 0.95 (d, *J* = 7 Hz, 3 H), 1.02 (s, 3 H), 1.17 (s, 3 H), 2.96 (s, 3 H), 4.06 (dd, *J* = 9.5, 6.2 Hz, 1 H), 4.17 (dd, *J* = 9.5, 4.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz)[31] δ 14.50 (q), 19.12 (t), 23.24 (t), 25.86 (t), 29.24 (q), 30.41 (q), 33.57 (s), 34.32 (d), 34.32 (t), 34.94 (d)*, 36.53 (t)*, 37.14 (q), 39.87 (t)*, 48.78 (d), 73.38 (t), 73.80 (s); mass spectrum *m/e* (relative intensity) 303 (M^+ - 15, 3), 300 (13), 285 (29), 207 (16), 204 (70), 189 (47), 137 (44), 109 (72), 95 (65), 81 (100); calcd for $C_{15}H_{27}O_4S$ (M^+ - 15) *m/e* 303.1630, found 303.1631.

[7*R*-[1α,4aα,7α(*S),8aα)]]-Decahydro-1-hydroxy-1,4a-dimethyl-7-(1-methyl-2-iodoethyl)naphthalene (34).** To a stirred solution of 0.441 g (1.39 mmol) of mesylate **33** in 20 mL of acetone was added 0.397 g (2.65 mmol) of NaI. The reaction mixture was heated at reflux for 48 h, allowed to come to room temperature, and then poured into 100 mL of water. The acetone was evaporated under reduced pressure, and the remaining aqueous layer was extracted with three 50-mL portions of EtOAc. The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (10:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 0.432 g (88%) of **34**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.86 (d, *J* = 6 Hz, 3 H), 0.90–1.80 (m, 16 H), 0.98 (s, 3 H), 1.18 (s, 3 H), 3.21 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz)[31] δ 18.46 (t), 18.56 (q), 19.14 (t), 23.25 (t), 25.83 (t), 29.38 (q), 30.45 (q), 33.53 (s), 34.75 (t), 35.92 (t)*, 37.16 (d), 37.16 (d), 39.53 (t)*, 48.66 (d), 73.87 (s); mass spectrum *m/e* (relative intensity) 335 (M^+ - 15, 3), 332 (11), 317 (19), 205 (50), 163 (79), 123 (21), 109 (43), 95 (49), 81 (74), 71 (100); calcd for $C_{14}H_{24}OI$ (M^+ - 15) *m/e* 335.0871, found 335.0867.

(+)-5-*epi*-Neointermedeol (11). To a stirred solution of 0.232 g (0.66 mmol) of iodide **34** in 20 mL of dry *t*-BuOH was added 1.00 g (8.91 mmol) of *t*-BuOK. The reaction mixture was heated at reflux for 9 h, allowed to come to room temperature, and then diluted with 100 mL of saturated aqueous NH_4Cl. The aqueous solution was extracted with three 50-mL portions of EtOAc. The combined organic layers were dried and evaporated. The remaining residue was flash chromatographed (15:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 0.144 g (98%) of **11**: $[\alpha]_D$ = +30.2 ± 0.1° (*c* = 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.05 (s, 3 H), 1.00–1.80 (m, 14 H), 1.23 (s, 3 H), 1.69 (d, *J* = 0.5 Hz, 3 H), 2.26 (m, 1 H), 4.73 (br s, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz)[31] δ 19.08 (t), 21.29 (q), 24.52 (t), 26.35 (t), 28.91 (q), 30.30 (q), 33.50 (s), 34.45 (t), 36.65 (t)*, 39.31 (d), 39.97 (t)*, 49.01 (d), 73.83 (s), 109.10 (t), 148.74 (s); mass spectrum *m/e* (relative intensity) 222 (M^+, 11), 207 (3), 204 (82), 189 (100), 175 (11), 161 (68), 147 (36), 135 (71), 121 (39), 109 (74), 95 (58), 81 (88), 71 (44); calcd for $C_{15}H_{26}O$ (M^+) *m/e* 222.1984, found 222.1994.

(+)-Amiteol (9). The same procedure was followed as described for the synthesis of (+)-**11**. The diol **35** (0.132 g, 0.55 mmol) gave, via its mesylate **36** and iodide **37**, (+)-**9** in 58% overall yield. The physical and spectroscopic data of **36**, **37**, and (+)-**9** are shown below.

36: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.88 (s, 3 H), 0.93 (d, *J* = 7 Hz, 3 H), 1.00–2.20 (m, 16 H), 1.19 (s, 3 H), 2.96 (s, 3 H), 4.14

(31) Coalescence was observed for the marked signals. Increasing the temperature leads to sharpening of these signals.

(d, J = 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.39 (q), 17.34 (t), 23.76 (t), 25.99 (t), 29.31 (q), 31.19 (q), 32.07 (t), 32.76 (s), 33.30 (d), 37.25 (q), 38.58 (d), 41.60 (t), 42.39 (t), 47.59 (d), 73.19 (s), 73.58 (t); mass spectrum m/e (relative intensity) 300 (M^+ - 18, 6), 285 (11), 205 (17), 189 (30), 163 (22), 137 (44), 121 (24), 109 (22), 95 (60), 81 (100); calcd for $C_{16}H_{28}O_3S$ (M^+ - 18) m/e 300.1759, found m/e 300.1748.

37: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.70-2.20 (m, 16 H), 0.88 (s, 3 H), 0.94 (m, 3 H), 1.26 (s, 3 H), 3.29 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.26 (t), 17.66 (q), 18.66 (t), 23.95 (t), 25.61 (t), 29.14 (q), 31.30 (q), 31.87 (t), 32.52 (s), 37.08 (d), 39.98 (d), 41.48 (t), 42.08 (t), 47.46 (d), 73.17 (s); mass spectrum m/e (relative intensity) 332 (M^+ - 18, 13), 317 (10), 205 (42), 163 (100), 135 (15), 123 (24), 109 (72), 95 (47), 81 (88), 71 (83); calcd for $C_{15}H_{25}I$ (M^+ - 18) m/e 332.1001, found 332.0984.

(+)-**9**: $[\alpha]_D$ = +17.7 ± 0.1°, $[\alpha]_{365}$ = +60.3 ± 0.1° (c = 1.2, $CHCl_3$) (lit.[4] $[\alpha]_{365}$ = +8° ($CHCl_3$)). The spectroscopic data of (+)-**9** were identical with those of (±)-**9**.

Acknowledgment. We would like to thank A. van Veldhuizen for recording ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra, and C. J. Teunis and H. Jongejan for mass spectral data and elemental analyses.

Abbreviations: NDC, nicotinium dichromate; Oxone, a mixture of $KHSO_5$, $KHSO_4$, and K_2SO_4 in the ratio of 2:1:1, respectively.

Registry No. (±)-**1**, 58844-48-7; (±)-**2**, 136391-44-1; (±)-**3**, 136391-49-6; (±)-**4**, 136391-47-4; (±)-**5**, 136734-22-0; (±)-**6**, 136777-50-9; (±)-**7**, 122674-22-0; (±)-**8**, 136734-23-1; (±)-**9**, 136734-24-2; (+)-**9**, 83378-02-3; (±)-**10**, 136734-25-3; (±)-**11**, 136734-26-4; (+)-**11**, 136734-27-5; (±)-**12**, 136734-28-6; (±)-**13**, 136631-02-2; (±)-**14**, 136631-03-3; (±)-**15**, 136631-04-4; (±)-**16**, 136631-05-5; (±)-(*E*)-**17a**, 136658-51-0; (±)-(*Z*)-**17a**, 136631-06-6; (±)-(*E*)-**17b**, 136631-07-7; (±)-(*Z*)-**17b**, 136631-08-8; (±)-**18a**, 136734-29-7; (±)-**18b**, 136734-30-0; (±)-**19a**, 136734-31-1; (±)-**19b**, 136734-32-2; (±)-(*E*)-**20**, 136631-09-9; (±)-(*Z*)-**20**, 136631-10-2; (±)-**21** (isomer 1), 136631-11-3; (±)-**21** (isomer 2), 136631-12-4; (±)-**22**, 136631-13-5; (±)-**23**, 136734-33-3; (±)-**24**, 136734-34-4; (±)-**25**, 136734-35-5; (±)-(*E*)-**26**, 136631-14-6; (±)-(*Z*)-**26**, 136631-15-7; (±)-**27**, 136734-36-6; (±)-**28**, 136734-37-7; **29**, 3466-64-6; **30**, 18172-87-7; **31**, 122421-95-8; **31** (epoxide, isomer 1), 136631-22-6; **31** (epoxide, isomer 2), 136734-39-9; **32**, 136631-16-8; **33**, 136631-17-9; **34**, 136631-18-0; **35**, 136631-19-1; **36**, 136631-20-4; **37**, 136631-21-5; (-)-α-santonin, 481-06-1.

Supplementary Material Available: NMR spectra (^{1}H and ^{13}C) for **5-12** and **25** (18 pages). Ordering information is given on any current masthead page.

E/Z Isomerization, Solvolysis, Addition, and Cycloaddition Reactions of (*E*)-*tert*-Butylketene Methyl *tert*-Butyldimethylsilyl Acetal

Waldemar Adam* and Xiaoheng Wang[1]

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, Germany

Received August 20, 1991

In the presence of catalytic amounts of CF_3COCH_3 or CF_3COCF_3, the silyl ketene acetal *E*-**1** was isomerized into its *Z* isomer (*Z*/*E* ratio 90:10). For this novel *E*/*Z* isomerization a mechanism is proposed, in which addition and reelimination of the fluoro ketone, through a 1,4-dipolar intermediate operates. With the protic nucleophiles CH_3OH, CF_3CH_2OH, or PhOH, the ketene acetal *E*-**1** afforded the ortho esters **2** as addition products, while CH_3CO_2H, CF_3CO_2H, or H_2O led to methyl pivalate as the solvolysis product. This chemistry is readily explained through protonation of the ketene acetal *E*-**1** to generate the corresponding carbenium ion. At low temperature the reaction with TCNE gave the silylketene imine **3** as labile cycloadduct, which underwent on workup desilylation to give the TCNE-incorporated ester **6**; the latter eliminated hydrogen cyanide at room temperature to give the ene ester **7**. With MTAD the labile silyl ene product **4** was obtained initially, which underwent silyl migration to give N-silylated urazole **8**; final desilylation led to the stable urazole **9**. Also for the ene reactions of TCNE and MTAD with the silyl ketene acetal *E*-**1**, a 1,4-dipolar intermediate is proposed to intervene.

Introduction

The cycloaddition chemistry of electron-rich olefins, particularly enol ethers, has been extensively investigated, mainly with the cyclophile tetracyanoethylene (TCNE)[2] but to some extent also with 1,2,4-triazoline-3,5-diones (TAD).[3] In a recent series of papers Huisgen and Brückner[4] employed 2,2-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (BTF) as enophile and confirmed earlier studies with TCNE[5] that the [2 + 2] cycloadducts are produced in a stepwise mechanism with a 1,4-dipole as a bona fide intermediate. Kinetics, solvent effect, and trapping experiments were used as mechanistic tools to establish rigorously the intervention of such dipolar species in these cycloaddition reactions.

Silyl ketene acetals, which, because of their high reactivity, serve as valuable building blocks in organic synthesis,[6] have received comparatively little attention as cycloaddition partners with such reactive cyclophiles. For example, we showed[7] that such ketene acetals afford with singlet oxygen α-silylperoxy esters. In this photooxygenation, at low temperature first the labile dioxetanes were produced exclusively and stereoselectively. Subsequently, on warming the dioxetanes opened up to the corresponding 1,4-dipole, and silatropic migration afforded the α-silylperoxy ester as a final product. This sequence

(1) This work was assisted by Nana Novak as undergraduate research participant in the IAESTE program (Jugoslavia).

(2) Fatiadi, A. J. *Synthesis* **1986**, *4*, 249; **1987**, *9*, 749; **1987**, *11*, 959.

(3) (a) Cookson, R. C.; Gupe, S. S.; Stevens, I. D.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121. (b) Adam, W.; DeLucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

(4) (a) Huisgen, R.; Brückner, R. *Tetrahedron Lett.* **1990**, *31*, 2553. (b) Brückner, R.; Huisgen, R. *Tetrahedron Lett.* **1990**, *31*, 2557, 2561.

(5) (a) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117, 199. (b) Huisgen, R.; Steiner, G. *J. Am. Chem. Soc.* **1973**, *95*, 5054, 5055. (c) Steiner, G.; Huisgen, R. *J. Am. Chem. Soc.* **1973**, *95*, 5056. (d) Huisgen, R.; Schug, R. *J. Chem. Soc., Chem. Commun.* **1975**, 59. (e) Schug, R.; Huisgen, R. *J. Chem. Soc., Chem. Commun.* **1975**, 60.

(6) Brownbridge, P. *Synthesis* **1983**, 1.

(7) (a) Adam, W.; del Fierro, J.; Quiroz, F.; Yany, F. *J. Am. Chem. Soc.* **1980**, *102*, 2127. (b) Wang, X.-H. Dissertation, University of Würzburg, 1990. (c) Adam, W.; Wang, X.-H. *J. Org. Chem.* **1991**, *56*, 4737.

0022-3263/91/1956-7244$02.50/0