and the suspension formed was filtered off. The residue was washed with pentane. The organic layer was separated, and the aqueous layer was extracted twice with pentane. The pentane layer was washed with water, dilute HCl, water, and dilute NaOH in that order and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Purification by flash column chromatography with 9:1 hexane/ethyl acetate (R_f 0.38) gave the product: 1.10 g (70% yield); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, J = 6 Hz, CH_3), 1.0–1.75 (m, 6 H, CH_2's), 2.48 (br t, 2 H, J = 5 Hz, CH_2CO), 6.55 (d, 1 H, J = 18 Hz, =CHCO), 7.0–7.6 (m, 6 H, C_6H_5CH); IR (Nujol) 3100, 3065, 3020, 1695, 1670, 1615, 980, 740, 680 cm^{-1}; mass spectrum, m/z 202 (M^+).

Some other compounds that were prepared by using this basic procedure are as follows.

Cinnamonitrile: 31% yield; ^{1}H NMR ($CDCl_3$) δ 5.70 (d, 1 H, J = 18 Hz, =CHCN), 7.0–7.45 (m, 6 H, C_6H_5CH); IR (neat) 3070, 3030, 2210, 1620, 965, 745, 680 cm^{-1}; mass spectrum, m/z 129 (M^+).

2-Methyl-5-vinylthiophene: 40% yield; ^{1}H NMR ($CDCl_3$) δ 2.66 (s, 3 H, CH_3), 4.73–5.36 (m, 3 H, vinyl), 6.40–6.86 (m, 2 H, thiophene); IR (neat) 3100, 3080, 2970, 2920, 2880, 1620, 1450 cm^{-1}; mass spectrum, m/z 124 (M^+).

Methyl *trans*-3-(2-*n*-propyl-3-benzofuryl)acrylate: 50% yield; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3 H, J = 6 Hz, CH_3), 1.67 (m, 2 H, CH_2CH_3), 2.78 (t, 2 H, J = 7 Hz, CH_2), 3.69 (s, 3 H, OCH_3), 6.45 (d, 1 H, J = 18 Hz, vinyl), 7.1–7.84 (m, 6 H, aryl and vinyl); IR (neat) 3020, 2970, 2880, 1720, 1635, 1580, 1455, 1435, 1300, 1270, 1170, 965, 850, 750 cm^{-1}; mass spectrum, m/z calc for $C_{15}H_{16}O_3$ 244.109 95, obsd 244.109 74.

Acknowledgment. We gratefully acknowledge the generous financial support of the National Institutes of Health (Grant GM24254) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, as well as the Department of Health, Education, and Welfare and Iowa State University for a Graduate and Professional Opportunities Fellowship for S.S.H. Johnson Matthey Inc. kindly provided the rhodium trichloride essential for this work.

Registry No. $ClRh(PPh_3)_2$, 14694-95-2; $PhCH{=}CH_2$, 100-42-5; *cis*-$PhCH{=}CH(CH_2)_3CH_3$, 15325-54-9; *trans*-$PhCH{=}CH(CH_2)_3CH_3$, 6111-82-6; PhHgCl, 100-56-1; $H_2C{=}CHBr$, 593-60-2; LiCl, 7447-41-8; Me_2SO, 67-68-5; HMPA, 680-31-9; DMF, 68-12-2; *p*-methylstyrene, 622-97-9; *p*-methoxystyrene, 637-69-4; *m*-nitrostyrene, 586-39-0; 2-methyl-5-vinylthiophene, 62485-03-4; *trans*-1-phenyl-1-octen-3-one, 29478-39-5; cinnamonitrile, 1885-38-7; dimethyl phenylmaleate, 29576-99-6; methyl *trans*-3-(2-*n*-propyl-3-benzofuryl)acrylate, 87226-83-3; di-*p*-tolylmercury, 537-64-4; *p*-anisylmercuric chloride, 3009-79-8; (*m*-nitrophenyl)mercuric chloride, 2865-17-0; 2-(chloromercuri)-5-methylthiophene, 87226-84-4; 3-(chloromercuri)-2-*n*-propylbenzofuran, 87226-85-5; *cis*-1-bromo-1-hexene, 13154-12-6; *trans*-1-iodo-1-hexene, 16644-98-7; *cis*-1-iodo-1-hexene, 16538-47-9; *trans*-1-iodoocten-3-one, 39178-64-8; *trans*-3-iodoacrylonitrile, 56017-69-7; dimethyl iodomaleate, 1600-35-7; methyl *trans*-3-iodoacrylate, 6213-88-3.

Stereospecific Synthesis of Selectively C-7-Acetalized Substituted 4aβ-Methyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-diones. A Short Total Synthesis of (±)-β-Eudesmol, (±)-β-Selinene, and (±)-β-Dictyopterol

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Received December 7, 1982

An efficient general method has been developed for the synthesis of 4aβ,8α-dimethyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione 7-ethylene acetals **1** and 4aβ-methyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione 7-dimethyl acetals **2**, which are important intermediates in the total synthesis of eudesmanes and other sesquiterpenes. With (substituted) 4aβ-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2-(3*H*)-ones **3** as the starting compounds, the 8-positions were hydroxylated by *m*-chloroperbenzoic acid oxidation of the corresponding dienol ethers **4** or dienol acetates **5**. The 8-hydroxy unsaturated ketones **6** and **7** were oxidized to enediones **11**. Reductions of **11** to the diones **12**, **13**, and **14** were accomplished by using titanium(III) chloride or hydrogen iodide. Isomerization of the C-1-unsubstituted 8-hydroxy enones **6** and **7** with hydrogen bromide gave the diones **12** and **14** directly. Selective acetalization using 2-butanone dioxolane or trimethyl orthoformate gave **1** and **2**, respectively. Compounds **2a** and **2e** were converted into the methylene ketones **18a** and **18e**. Peterson olefination of the carbonyl functions with methoxy(phenylthio)(trimethylsilyl)methyllithium (**19**) was used for the preparation of intermediate ketene *O,S*-acetals which were methanolized directly to a stereoisomeric mixture of the methyl esters **21a,e** and **22a,e**. Finally, these esters were converted into (±)-β-eudesmol, (±)-β-selinene, and (±)-β-dictyopterol.

In the last decade several different approaches have been applied to the synthesis of eudesmanes[1] and/or eudesmanolides.[1a,b,2] Most of the reported syntheses of this class of sesquiterpenes have started from the Wieland–Miescher ketone or its derivatives, which are readily available from Robinson annelations of 2-methylcyclohexanone or 2-methyl-1,3-cyclohexanedione. Further elaboration of the Wieland–Miescher ketone or its analogues to intermediates with structure **1** has been demonstrated not only in the synthesis of several eudesmanes[3] or eudesmanolides[4] but also in the synthesis of guaiazulenic ses-

(1) For an extensive review of the total synthesis of eudesmane sesquiterpenes through the middle of 1970 see: (a) Heathcock, C. H. In "The Total Synthesis of Natural Products"; ApSimon, J., Ed.; Wiley: New York, 1973, Vol. II, Chapter 2. For the period 1970–1978 see: (b) *Terpenoids Steroids* **1971–1979**, *1–9*. (Chemical Society Specialists Periodical Reports). Recent reports on the synthesis of eudesmanes: (c) Cooper, J. L.; Harding, K. E. *Tetrahedron Lett.* **1977**, 3321. (d) Mackenzie, B. D.; Angelo, M. M.; Wolinsky J. *J. Org. Chem.* **1979**, *44*, 4042. (e) Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 6289. (f) Torii, S.; Inokuchi, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2642. (g) Miller, R. B.; Frincke, J. M. *J. Org. Chem.* **1981**, *46*, 2972.

(2) Schultz, A. G.; Godfrey, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 2414 and references herein.

(3) (a) Marshall, J. A.; Pike, M. T.; Carroll, R. D. *J. Org. Chem.* **1966**, *31*, 2933. (b) Posner, G. H.; Loomis, G. L.; Sawaya, H. S. *Tetrahedron Lett.* **1975**, 1373. (c) Vig, O. P.; Sharma, M. L.; Anand, R.; Sharma, S. D. *J. Indian Chem. Soc.* **1976**, *53*, 81. (d), Vig, O. P.; Kumar, S. D.; Vig, R.; Sharma, S. D. *Indian J. Chem.* **1980**, *19B*, 871.

(4) (a) Minato, H.; Nagasaki, T. *J. Chem. Soc. C* **1968**, 621. (b) Grieco, P. A.; Nishizawa, M. *J. Chem. Soc., Chem. Commun.* **1976**, 582. (c) Nishizawa, M.; Grieco, P. A.; Burke, S. D.; Metz, W. *Ibid.* **1978**, 76.

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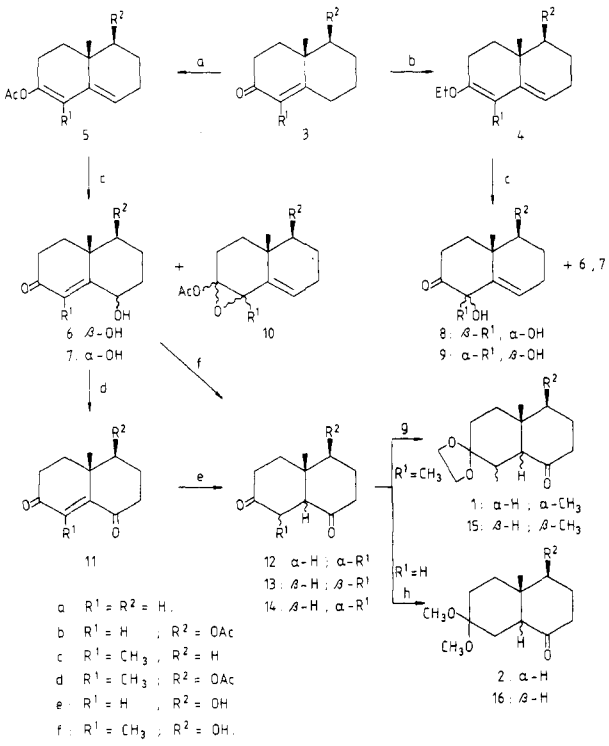
Scheme I[a]



[a] (a) Ac_2O, H^+; (b) $(EtO)_3CH$, H^+; (c) MCPBA; (d) pyridine, CrO_3, HCl/alumina; (e) $TiCl_3$ or HJ; (f) HBr; (g) MED, H^+; (h) $(CH_3O)_3CH$, H^+.

Table I. *m*-Chloroperbenzoic Acid Oxidation of Ethyl Dienol Ethers 4

reactant 4	reaction time, h	products,[a] % 6	7	8	9
a	4	50[b]	17.5[b]		
b	2	39	13		
c	4	16	6	49	4.5
d	1	12[c]	5[c]	40.5	7.5

[a] Isolated yield after column chromatography. [b] See ref 11c. [c] Product ratio according to GLC.

quiterpenoids[5] and *trans*-perhydroindanones.[6] In the present paper we report an effective and potentially general methodology for the synthesis of **1** and its analogue **2**. The transformation of **2a** and **2e** via a Peterson olefination to (±)-β-eudesmol (**23a**),[7] (±)-β-selinene (**25a**),[8] and (±)-β-dictyopterol (**25e**)[9] is also described.

Results and Discussion

Since we wanted to develop a general and effective synthetic route we selected the easy accessible enones **3a–d** as starting materials. The conversion of these enones, all of them prepared according to standard Robinson annelation procedures, into **1** and **2** is outlined in Scheme I. The hydroxylation of the C-8 position[10] in the enones was investigated via oxidation of the dienol ethers **4** and the dienol acetates **5**. Conversion of the enones **3** into the ethyl dienol ethers **4** proceeded in almost quantitative yield. When R^1 = H the results of the *m*-chloroperbenzoic acid oxidation[11] were in full agreement with those reported in the literature[11c] (Table I). However, when $R^1 = CH_3$, the C-1-hydroxylated products **8c,d** and **9c,d** were predominantly formed, probably as a result of the "peri" steric effect[12] of the C-1 methyl group. The stereochemistry of the alcohols **8** and **9** was assigned on the basis of a rather pronounced change in the ^1H NMR chemical shift of both angular methyl signals in **8c** and **9c** (Table II) when the spectra in carbon tetrachloride and pyridine-d_5 were compared.[13] The unfavorable course of the *m*-chloroperbenzoic acid oxidation of the ethyl dienol ethers **4c** and **4d** prompted us to investigate the oxidation of the corresponding dienol acetates **5a–d**. The enones **3a–d** were converted into their dienol acetates by treatment with acetic anhydride in the presence of a catalytic amount of concentrated sulfuric acid.[14] The procedure for the oxidation of ethyl dienol ethers was also employed for the dienol acetates **5a–d**[15] (Table III). Examination of Tables II and III clearly shows that at least when $R^1 = CH_3$, the dienol acetates were the appropriate starting compounds in the *m*-chloroperbenzoic acid oxidation. The subsequent step was the conversion of the enones **6** and **7** into the trans-fused diones **12**. Catalytic reduction of **6** or **7** afforded complex reaction mixtures and lithium ammonia

Table II. Methyl Chemical Shifts for Compounds 8c and 9c

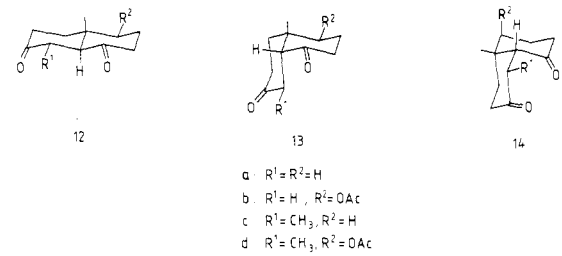
	^1H NMR, δ			
	in CCl_4		in pyridine-d_5	
compd	C-4a methyl	C-1 methyl	C-4a methyl	C-1 methyl
8c	1.32	1.39	1.22	1.60
9c	0.92	1.30	1.17	1.54

Table III. *m*-Chloroperbenzoic Acid Oxidation of Dienol Acetates 5

reactant 5	reaction time, h	products,[a] % 6	7	10
a	16	57[b]	18[b]	
b	24	51	17	
c	16	62	25	7
d	16	57[c]	28[c]	12

[a] Isolated yield after column chromatography. [b] See ref 11c. [c] Product ratio according to GLC.

Chart I



a $R^1 = R^2 = H$
b $R^1 = H$, $R^2 = OAc$
c $R^1 = CH_3$, $R^2 = H$
d $R^1 = CH_3$, $R^2 = OAc$

(5) Heathcock, C. H.; Ratcliffe, R. *J. Am. Chem. Soc.* **1971**, *93*, 1746.
(6) Dawson, T. M.; Littlewood, P. S.; Lythgoe, B.; Medcalfe, T.; Moon, M. W.; Tomkins, P. M. *J. Chem. Soc. C* **1971**, 1292.
(7) Miller, R. B.; Nash, R. D. *J. Org. Chem.* **1973**, *38*, 4424 and references herein.
(8) See ref 1d and references herein.
(9) Kurosawa, E.; Izawa, M.; Yamamoto, K.; Masamune, T.; Irie, T. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2509.
(10) The numbering system follows the IUPAC designations used in the Experimental Section.
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(13) (a) Demarco, P. V.; Farkas, E.; Doddrell, D.; Mylari, B. L.; Wenkert, E. *J. Am. Chem. Soc.* **1968**, *90*, 5480. (b) Huffman, J. W.; Zalkow, L. H. *Tetrahedron Lett.* **1973**, 751.
(14) Nakazaki, M.; Naemura, K. *Tetrahedron Lett.* **1966**, 2615.
(15) The use of *m*-chloroperbenzoic acid in 2-propanol/water (20:1) caused about 40% hydrolysis of the dienol acetate in a similar reaction. See: Caine, D.; Deutsch, H. *J. Am. Chem. Soc.* **1978**, *100*, 8030.

Table IV. Titanium(III) Chloride and Hydrogen Iodide Reduction of Enediones 11

	titanium(III) chloride					hydrogen iodide				
			products,[b] %					products,[b] %		
reactant	reaction time, h	reductant,[a] mL	12	13	14	reaction time, h	reductant,[a] mL	12	13	14
11a	1	2	65		29[c]	2	0.7	65		32[c]
11b	1	2	64		31	2	0.7	66		28
11c	2	3	38.5	45.5	11	6.5	1.7	73.5	16	7.5
11d	3	4	78[d]	20[d]		6.5	1.7	87[d]	10[d]	

[a] Milliliters of reductant/millimole of reactant. [b] Isolated yield after column chromatography. [c] See ref 3a. [d] Product ratio according to ^{1}H NMR.

reduction caused elimination of the hydroxyl group from the 8-β-hydroxy enone **6a**.[16] Therefore, we decided to attempt the reduction of the double bond after oxidation of the C-8 hydroxy group. Oxidation of enones **6** and **7**, or mixtures of them, with pyridinium chlorochromate adsorbed on alumina[17] gave lower yields in those cases in which R^1 = H relative to those in which R^1 = CH_3. Probably some overoxidation occurred in the former cases which was supported by the comparative instability of **11a** and **11b** which darkened upon standing at room temperature. A direct acid-catalyzed isomerization of **6a,b** and **7a,b** into **12a,b** and **14a,b** circumvented this problem (vide infra).

For the reduction of the double bond, titanium(III) chloride[18] and sodium iodide/concentrated hydrogen chloride[19] were investigated. The sodium iodide/concentrated hydrogen chloride method proceeded incompletely and sluggishly in case of **11c** and **11d**. Consideration of the proposed mechanism prompted us to use an aqueous 57% hydrogen iodide solution and in this manner excellent results were obtained (Table IV). The titanium(III) chloride and hydrogen iodide treatment of the enediones **11a** and **11b** both afforded a 2:1 mixture of trans and cis diones **12a,b** and **14a,b** respectively (Chart I). The cis nonsteroid conformation of **14a** and **14b** was revealed from the ^{1}H NMR spectra.[20]

The reduction of the enediones **11c** and **11d** gave a more complex picture. Treatment of **11c** with titanium(III) chloride afforded a mixture of three isomers, easily separated by column chromatography, giving **12c**, **13c**, and **14c** in 38.5%, 45.5%, and 11% yields, respectively.[21] The trans dione **12d** was formed by preference when **11d** was treated with titanium(III) chloride. Reduction of **11c** and **11d**[22] with hydrogen iodide afforded predominantly **12c** and **12d**, respectively, in high yields. The distinction of the cis nonsteroid dione **14c** and the other isomers **12c** and **13c** became obvious from the ^{1}H NMR spectra.[20] Because of the great similarity in the ^{1}H NMR spectra of **12c** and **13c** the stereochemical assignment of these compounds were elucidated by ^{13}C NMR studies. The ^{13}C shielding data for the angular methyl group of **12c**, **13c**, and **14c** were 16.90, 26.44, and 26.66 ppm, respectively. These data confirmed our stereochemical assignments concerning the ring junction.[23] On consideration of the ^{13}C NMR chemical shifts of C-8a of **12c**, **13c**, and **14c** (63.37, 66.44, and 63.31 ppm, respectively) the position of the C-8 methyl group was assumed to be equatorial.[24]

The modest yields of **11a** and **11b** in the oxidation reaction with pyridinium chlorochromate adsorbed on alumina prompted us to investigate an alternative route. It appeared that treatment of a mixture of **6a** and **7a** with concentrated hydrogen bromide afforded the diones **12a** and **14a** as a 2:1 mixture, respectively, in 85% yield. In a similar way a mixture of **6b** and **7b** gave the diones **12b** and **14b** in the same ratio in nearly quantitative yield. When **6d** or other C-1-*methylated* 8-hydroxy enones were treated with concentrated hydrogen bromide, the expected diones were found only in modest yield. It appeared that a dehydration had occurred during the reaction in about 30%.

It is known that the formation of dialkyl acetals using orthoformates is generally restricted to aldehydes and unhindered ketones.[25] Reaction of a mixture of **12a** and **14a** with trimethyl orthoformate in the presence of *p*-toluenesulfonic acid monohydrate at room temperature in ether gave the C-7-acetalized compounds **2a** and **16a** in 72% yield. Similar results were found when a mixture of **12b** and **14b** was treated with trimethyl orthoformate. In both cases no bis acetals or C-1-acetalized products were formed.[3a] Treatment of a mixture of **2a** and **16a** or a mixture of **2b** and **16b** with methanolic sodium methoxide caused complete epimerization, leading to pure **2a** or **2e**, respectively.[26] In contrast to the C-8 unsubstituted diones the C-8-methylated diones **12c** and **12d** gave excellent yields of the corresponding C-7-acetalized compounds upon treatment with 2-butanone dioxolane. In this manner **1c**[4b,c] and **1d** could be isolated in 93% and 100% yield, respectively. In the same way the cis-fused dione **13c** (steroid conformation) afforded **15c** also in high yield (90%), although the reaction time was much longer than for the trans compound **12c**. The cis-fused dione **14c** (nonsteroid conformation) could not be transformed into a dioxolane.

(±)-β-Eudesmol, (±)-β-Selinene, and (±)-β-Dictyopterol. For the synthesis of (±)-β-eudesmol (**23a**) and (±)-β-selinene (**25a**) it was necessary to convert **2a** into the corresponding methylene derivative **17a** (Scheme II). In agreement with the results of Marshall[3a] treatment of a mixture of **2a** and its cis-fused epimer **16a** with methylenetriphenylphosphorane in dimethyl sulfoxide[27] and

(16) (a) Stork, G.; Logush, E. W. *J. Am. Chem. Soc.* **1980**, *102*, 1218. (b) de Groot, A.; Jansen, B. J. M.; Peterse, A. G. J. M.; Wijnberg, J. B. P. A. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 177.
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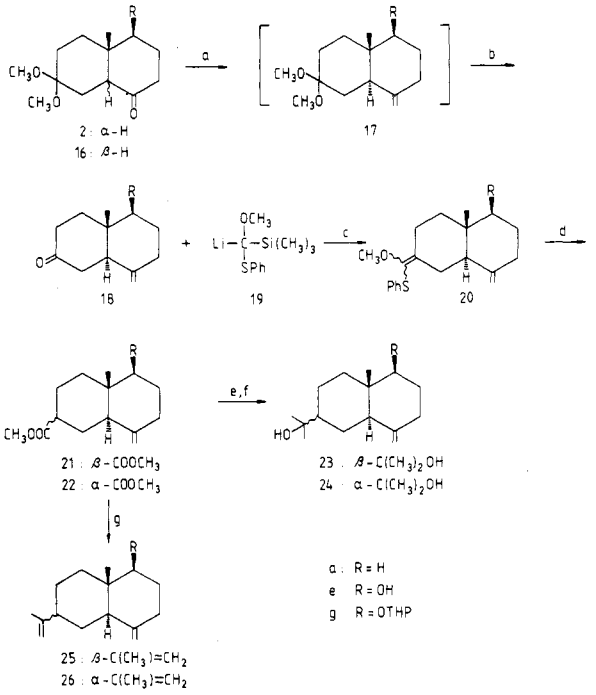
(20) (a) Williamsen, K. L.; Sloan, L. R.; Howell, T.; Spencer, T. A. *J. Org. Chem.* **1966**, *31*, 436. (b) House, H. O.; Lusch, M. J. *Ibid.* **1977**, *42* 183.
(21) Stork obtained the isomers **12c**, **13c**, and **14c** in yields of 19%, 25%, and 19% after reductive alkylation of **11a** (see ref 16a).
(22) Treatment of **11d** with zinc powder in refluxing acetic acid gave a mixture of **12d**, **13d**, and **14d** in yields of 35%, 45%, and 12%, respectively.
(23) (a) Birnbaum, G. J.; Stoessl, A.; Grover, S. H.; Stothers, J. B. *Can. J. Chem.* **1974**, *52*, 993. (b) Ayer, W. A.; Browne, L. M.; Fung, S.; Stothers, J. B. *Org. Magn. Reson.* **1978**, *11*, 73. (c) Browne, L. M.; Klinck, R. E.; Stothers, J. B. *Ibid.* **1979**, *12*, 561. (d) Caine, D.; Smith, T. L., Jr.; *J. Org. Chem.* **1978**, *43*, 755.
(24) Levy, G. C.; Nelson, G. L. In "Carbon-13 Nuclear Magnetic Resonance for Organic Chemistry"; Wiley-Interscience: New York, 1972; p 44.
(25) "Protective Groups in Organic Chemistry"; McOmie, J. F. W., Ed.; Plenum Press: London and New York, 1973; Chapter 9, p 327.
(26) Sondheimer, F.; Wolfe, S. *Can. J. Chem.* **1959**, *37*, 1870.
(27) Greenwald, R.; Chaykovski, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.

Scheme II[a]



[a] (a) $Ph_3P{=}CH_2$, Me_2SO; (b) H_3^+O, acetone; (c) THF, −80 °C; (d) H^+, $HgCl_2$, CH_3OH; (e) $NaOCH_3$, CH_3OH, Δ; (f) CH_3Li; (g) salt-free $Ph_3P{=}CH_2$ or DHP, PPTS; salt-free $Ph_3P{=}CH_2$; PPTs, 55 °C.

subsequent hydrolysis of the acetal **17a** gave the methylene ketone **18a** in 83% yield. The isopropyl side chain can best be introduced via an ester function, and we have developed for that purpose a new method for ester homologation of aldehydes and ketones via ketene *O,S*-acetals. The intermediate ketene *O,S*-acetals were prepared via a Peterson olefination[28] by using methoxy(phenylthio)(trimethylsilyl)methyllithium (**19**).[29] Addition of a solution of **18a** in tetrahydrofuran to a solution of **19** in the same solvent at −80 °C gave a mixture of stereoisomeric ketene *O,S*-acetals **20a**. These ketene *O,S*-acetals **20a** were methanolized directly with a 5% solution of 6 N hydrogen chloride in methanol in the presence of 1 equiv of mercury(II) chloride at room temperature to an 1.2:1 mixture of the esters **21a** and **22a** in 82% yield.[31] Equilibration of this mixture by using sodium methoxide in dry methanol for 60 h gave a mixture consisting of 87.5% of **21a** and 12.5% of **22a**, which after treatment with methyllithium afforded (±)-β-eudesmol (**23a**) in high yield, together with a minor quantity of its epimer **24a**.[32]

Treatment of the 1.2:1 mixture of **21a** and **22a** with 8–9 equiv of salt-free methylenetriphenylphosphorane[33] in tetrahydrofuran at reflux temperature gave a 45% yield of a colorless oil (71% based on converted starting material), which according to GCMS and ^1H NMR analysis[34] was pure (±)-β-selinene (**25a**).

The procedure outlined above for the synthesis of (±)-β-selinene was also employed in the synthesis of (±)-β-dictyopterol (**25e**). This sesquiterpene is a member of the 1-oxygenated subclass of the eudesmanes which has recently received considerably synthetic attention.[35] Treatment of **2e** with methylenetriphenylphosphorane and subsequent hydrolysis afforded **18e** in 89% yield. Conversion of **18e** into an 1.2:1 mixture of the corresponding epimeric esters **21e** and **22e** via ketene *O,S*-acetal **20e** was achieved in 77% overall yield. The desired conversion of the ester function of **21e** and **22e** into an isopropenyl group required protection of the hydroxyl group of **21e** and **22e** as its tetrahydropyranyl ether.[36] The ethers **21g** and **22g** were obtained in quantitative yield also in an 1.2:1 ratio. Reaction of this mixture of **21g** and **22g** with salt-free methylenetriphenylphosphorane and 1 equiv of methyltriphenylphosphonium bromide as a proton donor[33] in benzene at reflux temperature gave an 80% yield of the tetrahydropyranyl ether of (±)-β-dictyopterol (**25g**).[37] Hydrolysis of the tetrahydropyranyl ether function of **25g** with pyridinium *p*-toluenesulfonate in ethanol at 55 °C[36] gave (±)-β-dictyopterol (**25e**)[39] in 84% yield.

Experimental Section

Boiling points and melting points are uncorrected. ^1H NMR spectra were determined on a Varian EM-390 or a Hitachi Perkin-Elmer R-24B spectrometer. Chemical shifts are reported in δ units from the internal standard tetramethylsilane in chloroform-*d* as the solvent, unless otherwise noted. ^{13}C NMR spectra were recorded with a Varian XL-100 spectrometer in the pulse FT mode by using chloroform-*d* as the solvent and tetramethylsilane as the internal standard. Mass spectral data and exact mass measurements were obtained with AEI MS 902 and VG Micromass 7070F spectrometers. GC Analyses were carried out on a Varian 3700 chromatograph. The column used for determining product ratio was a 2-m column packed with 3% SP-2250 on Chromosorb W. Solvents were dried with anhydrous sodium sulfate prior to evaporation of the solvent under reduced pressure by using a rotary evaporator.

Starting Materials. The enones **3a**[40] and **3c**[4b] were prepared as described. The enones **3b** and **3d** were prepared by treating **3e**[41] and **3f**,[42] respectively, with a 2:1 mixture of pyridine and acetic anhydride according to the literature.[5]

Ethyl Dienol Ethers 4a–d. General Procedure. A mixture of 25 mmol of **3**, 10 mL of triethyl orthoformate, 5 mL of ethanol, and a catalytic amount of *p*-toluenesulfonic acid monohydrate

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(29) This reagent was prepared by reaction of methoxy(phenylthio)-methyllithium[30] with chlorotrimethylsilane at −80 °C, followed by deprotonation with *n*-butyllithium.

(30) (a) Trost, B. M.; Miller, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 7182. (b) de Groot, A.; Jansen, B. J. M. *Tetrahedron Lett.* **1981**, *22*, 887.

(31) An advantage of ketene *O,S*-acetals is their easy methanolysis to esters, which might be favorable when exocyclic double bonds, which are susceptible to isomerization, are present in the molecule.

(32) Kodama, M.; Shimada, K.; Itô, S. *Tetrahedron Lett.* **1981**, *22*, 1523.

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(37) During this reaction a minor quantity of **26g** was formed. After hydrolysis of the tetrahydropyranyl ether function a stereoisomer of (±)-β-dictyopterol was isolated. Comparison of the ^1H NMR spectrum of this compound **26e** [^1H NMR δ 0.73 (s, 3 H), 1.15–2.50 (m, 13 H) 1.72 (br s, 3 H) 3.40 (dd, J = 5, 12 Hz, 1 H) 4.50 (br s, 1 H) 4.75 (br s, 1 H) 4.85 (m, 2 H)] with that of 5β*H*-7β,10α-selina-4(14),11-diene[38] led to the establishment of its stereochemistry.

(38) Govindachari, T. R.; Parthasarathy, P. C.; Desai, H. K.; Mohamed, P. A. *Ind. J. Chem.* **1973**, *11*, 971.

(39) In a reinvestigation of the constituents of *Dictyopteris divaricata* no β-dictyopterol (**25e**) could be detected. See: Suzuki, M.; Kowata, N.; Kurosawa, E. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2366.

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was stirred at room temperature for 24 h. The reaction mixture was poured into saturated sodium bicarbonate and extracted with petroleum ether (bp 40–60 °C; 3 × 50 mL). The combined organic layers were washed with brine and dried. Filtration and evaporation under reduced pressure afforded the crude ethyl dienol ethers **4** (100%). These compounds were somewhat unstable and were used immediately without further purification.

2-Ethoxy-4aβ-methyl-3,4,4a,5,6,7-hexahydronaphthalene (4a):[11c] ^{1}H NMR δ 1.01 (s, 3 H), 1.27 (t, J = 7 Hz, 3 H), 1.30–2.40 (m, 10 H), 3.75 (q, J = 7 Hz, 2 H), 5.10 (br s, 1 H), 5.18 (t, J = 3.5 Hz, 1 H).

5β-Acetoxy-2-ethoxy-4aβ-methyl-3,4,4a,5,6,7-hexahydronaphthalene (4b):[43] ^{1}H NMR δ 1.08 (s, 3 H), 1.29 (t, J = 7 Hz, 3 H), 1.40–2.50 (m, 8 H), 2.06 (s, 3 H), 3.77 (q, J = 7 Hz, 2 H), 4.77 (dd, J = 7,8 Hz, 1 H), 5.16 (m, 2 H).

1,4aβ-Dimethyl-2-ethoxy-3,4,4a,5,6,7-hexahydronaphthalene (4c): ^{1}H NMR δ 0.99 (s, 3 H) 1.23 (t, J = 7 Hz, 3 H), 1.30–2.50 (m, 10 H), 1.71 (t, J = 1,5 Hz, 3 H), 3.76 (q, J = 7 Hz, 2 H), 5.36 (t, J = 3.5 Hz, 1 H).

5β-Acetoxy-1,4aβ-dimethyl-2-ethoxy-3,4,4a,5,6,7-hexahydronaphthalene (4d): ^{1}H NMR δ 1.05 (s, 3 H) 1.25 (t, J = 7 Hz, 3 H) 1.40–2.50 (m, 8 H) 1.71 (t, J = 1.5 Hz, 3 H), 2.05 (s, 3 H), 3.78 (q, J = 7 Hz, 2 H), 4.71 (dd, J = 7,8 Hz, 1 H), 5.35 (t, J = 3.5 Hz, 1 H).

Dienol Acetates 5a–d. General Procedure. The enones **3** (25 mmol) were treated with acetic anhydride according to the procedure as described by Nakazaki.[14] The reaction mixture was concentrated in vacuo, dissolved in 50 mL of an 1:1 mixture of petroleum ether (bp 40–60 °C) and ether, washed with saturated sodium bicarbonate and brine, and dried. Filtration and evaporation under reduced pressure afforded a brown oil which was purified by column chromatography on basic Woelm alumina (activity I) with petroleum ether bp (40–60 °C)/ethyl acetate 15/1. The so-obtained dienol acetates **5** (80%) were used immediately for the next reaction.

2-Acetoxy-4aβ-methyl-3,4,4a,5,6,7-hexahydronaphthalene (5a): ^{1}H NMR δ 1.05 (s, 3 H), 1.30–2.60 (m, 10 H), 2.10 (s, 3 H), 5.35 (t, J = 3.5 Hz, 1 H), 5.65 (br s, 1 H).

2,5β-Diacetoxy-4aβ-methyl-3,4,4a,5,6,7-hexahydronaphthalene (5b): ^{1}H NMR δ 1.10 (s, 3 H), 1.30–2.50 (m, 8 H), 2.04 (s, 3 H), 2.10 (s, 3 H), 4.76 (dd, J = 7,8 Hz, 1 H), 5.37 (t, J = 3.5 Hz, 1 H), 5.72 (br s, 1 H).

2-Acetoxy-1,4aβ-dimethyl-3,4,4a,5,6,7-hexahydronaphthalene (5c): ^{1}H NMR δ 1.04 (s, 3 H), 1.30–2.60 (m, 10 H), 1.61 (t, J = 1.5 Hz, 3 H), 2.14 (s, 3 H), 5.58 (t, J = 3.5 Hz, 1 H).

2,5β-Diacetoxy-1,4aβ-dimethyl-3,4,4a,5,6,7-hexahydronaphthalene (5d): ^{1}H NMR δ 1.10 (s, 3 H), 1.30–2.65 (m, 8 H), 1.61 (t, J = 1.5 Hz, 3 H), 2.03 (s, 3 H), 2.12 (s, 3 H), 4.72 (dd, J = 7,8 Hz, 1 H), 5.52 (t, J = 3.5 Hz, 1 H).

***m*-Chloroperbenzoic Acid Oxidation. General Procedure.** A solution of 30 mmol of 85% *m*-chloroperbenzoic acid in a mixture of 100 mL of dioxane and 100 mL of buffer (pH 8)[44] was added over a period of 1 h to a stirred solution of 25 mmol of dienol compound **4** or **5** in a mixture of 100 mL of dioxane and 100 mL of buffer (pH 8) at 0 °C. Stirring was continued at room temperature for 1–24 h. After addition of 5.0 g of sodium thiosulphate and 10.0 g of sodium bicarbonate the reaction mixture was stirred for 15 min, poured into water, and extracted with dichloromethane (4 × 100 mL). The combined organic layers were washed with brine and dried. Filtration and evaporation under reduced pressure afforded the crude reaction mixtures. Column chromatography on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (5:1 to 1:1) gave the pure compounds. Experimental details and yields are listed in Table I and Table III for ethyl dienol ethers **4** and dienol acetates **5**, respectively.

8β-Hydroxy-4aβ-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (6a). Compound **6a** had identical spectral characteristics with those reported in the literature.[11c]

5β-Acetoxy-8β-hydroxy-4aβ-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (6b): mp 149–151 °C (from diisopropyl ether); ^{1}H NMR δ 1.40–2.82 (m, 8 H), 1.50 (s, 3 H), 2.11 (s, 3 H), 3.27 (br s, 1 H), 4.31 (t, J = 2 Hz, 1 H), 4.67 (dd, J = 4, 10 Hz, 1 H), 5.89 (s, 1 H); mass spectrum, m/e (relative intensity) 238 (M^+, 4), 196 (77), 178 (35), 150 (23), 139 (28), 118 (28). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.52; H, 7.61. Found: C, 65.81; H, 7.77.

1,4aβ-Dimethyl-8β-hydroxy-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (6c): mp 89–91 °C (from petroleum ether (bp 40–60 °C)/ether); ^{1}H NMR δ 1.35–2.92 (m, 10 H), 1.41 (s, 3 H), 1.82 (s, 3 H), 2.51 (br s, 1 H), 4.92 (t, J = 2 Hz, 1 H); mass spectrum, m/e (relative intensity) 194 (M^+, 100), 176 (31), 161 (52), 151 (32), 137 (59), 123 (70). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.42; H, 9.26.

5β-Acetoxy-1,4aβ-dimethyl-8β-hydroxy-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (6d). *m*-Chloroperbenzoic acid oxidation of **4d** or **5d** afforded after column chromatography on silica gel a fraction, which, according to ^{1}H NMR, was a 2:1 mixture of **6d** and **7d** [**7d**: ^{1}H NMR (major peaks) δ 1.24 (s, 3 H) 1.90 (s, 3 H)] and could not be separated further by preparative chromatography. Recrystallization from petroleum ether (bp 80–100 °C)/ether gave pure **6d**: mp 115–117 °C; ^{1}H NMR δ 1.40–2.70 (m, 8 H), 1.44 (s, 3 H), 1.84 (s, 3 H), 2.09 (s, 3 H), 2.94 (br s, 1 H), 4.60 (dd, J = 3, 11 Hz, 1 H), 4.90 (t, J = 2 Hz, 1 H); mass spectrum, m/e (relative intensity) 252 (M^+, 15), 210 (86), 192 (35), 164 (28), 149 (31), 136 (26). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.87; H, 7.74.

8α-Hydroxy-4aβ-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (7a). Compound **7a** had identical spectral characteristics with those reported in the literature.[11c]

5β-Acetoxy-8α-hydroxy-4aβ-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (7b): mp 153–155 °C (from diisopropyl ether); ^{1}H NMR δ 1.28 (s, 3 H) 1.40–2.70 (m, 8 H), 2.08 (s, 3 H), 3.18 (br s, 1 H), 4.38 (m, 1 H) 4.68 (dd, J = 5, 10 Hz, 1 H), 6.22 (d, J = 2 Hz, 1 H); mass spectrum, m/e (relative intensity) 238 (M^+, 5), 196 (86), 178 (44), 150 (24), 139 (30), 118 (22). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.52; H, 7.61. Found: C, 65.28; H, 7.71.

1,4aβ-Dimethyl-8α-hydroxy-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (7c): mp 70–72 °C (from petroleum ether (bp 40–60 °C)/ether); ^{1}H NMR δ 1.20 (s, 3 H), 1.35–2.77 (m, 10 H), 1.91 (s, 3 H), 2.90 (br s, 1 H), 4.71 (t, J = 4 Hz, 1 H); mass spectrum, m/e (relative intensity) 194 (M^+, 48), 176 (86), 161 (60), 151 (61), 137 (53), 123 (100). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.47; H, 9.33.

1,4aβ-Dimethyl-1α-hydroxy-3,4,4a,5,6,7-hexahydronaphthalen-2(1*H*)-one (8c): mp 39–41 °C (from pentane); ^{1}H NMR δ (CCl_4) 1.32 (s, 3 H), 1.39 (s, 3 H), 1.40–2.50 (m, 9 H), 2.83 (dt, J = 6, 14 Hz, 1 H), 3.62 (br s, 1 H), 6.00 (t, J = 3.5 Hz, 1 H); mass spectrum, m/e (relative intensity) 194 (M^+, 1), 179 (7), 176 (6), 151 (100). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.90; H, 9.29.

5β-Acetoxy-1,4aβ-dimethyl-1α-hydroxy-3,4,4a,5,6,7-hexahydronaphthalen-2(1*H*)-one (8d): mp 68–70 °C (from petroleum ether (bp 40–60 °C)); ^{1}H NMR δ 1.38 (s, 3 H), 1.40–3.20 (m, 8 H), 1.49 (s, 3 H), 2.04 (s, 3 H), 3.85 (br s, 1 H), 4.63 (dd, J = 7, 8 Hz, 1 H), 5.98 (t, J = 3.5 Hz, 1 H); mass spectrum, m/e (relative intensity) 252 (M^+, 1), 234 (3), 149 (79). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.78; H, 8.11.

1,4aβ-Dimethyl-1β-hydroxy-3,4,4a,5,6,7-hexahydronaphthalen-2(1*H*)-one (9c): mp 61–63 °C (from pentane); ^{1}H NMR δ (CCl_4) 0.92 (s, 3 H), 1.30 (s, 3 H), 1.37–2.23 (m, 8 H), 2.47–2.70 (m, 2 H), 3.33 (br s, 1 H), 5.80 (t, J = 3.5 Hz, 1 H); mass spectrum, m/e (relative intensity) 194 (M^+, 6), 179 (10), 176 (7), 151 (100). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.48; H, 9.35.

5β-Acetoxy-1,4aβ-dimethyl-1β-hydroxy-3,4,4a,5,6,7-hexahydronaphthalen-2(1*H*)-one (9d): mp 120–122 °C (from diisopropyl ether); ^{1}H NMR δ 1.00 (s, 3 H), 1.44 (s, 3 H), 1.50–2.90 (m, 8 H), 2.08 (s, 3 H), 3.78 (br s, 1 H), 4.82 (dd, J = 7, 8 Hz, 1 H), 5.95 (t, J = 3.5 Hz, 1 H); mass spectrum, m/e (relative intensity) 252 (M^+, 1) 224 (3), 192 (9), 149 (36). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.65. H, 8.15.

2-Acetoxy-1,4aβ-dimethyl-1β,2β-epoxy-1,2,3,4,4a,5,6,7-octahydronaphthalene (10c): colorless oil, which crystallized upon standing in a refrigerator; ^{1}H NMR δ 1.24 (s, 3 H), 1.50 (s, 3 H), 1.50–2.95 (m, 10 H), 2.03 (s, 3 H), 5.72 (t, J = 3.5 Hz, 1 H); mass spectrum, m/e (relative intensity) 236 (M^+, 3), 194 (46), 176 (47), 161 (28), 151 (100). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H,

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8.53. Found: C, 71.42; H, 8.44.

2,5β-Diacetoxy-1,4aβ-dimethyl-1β,2β-epoxy-1,2,3,4,4a,5,6,7-octahydronaphthalene (10d): mp 132–134 °C (from petroleum ether (bp 80–100 °C)); ^{1}H NMR δ 1.30 (s, 3 H), 1.50 (s, 3 H), 1.60–2.90 (m, 8 H), 2.10 (s, 6 H), 4.80 (t, J = 8 Hz, 1 H), 5.78 (t, J = 3.5 Hz, 1 H); mass spectrum, m/e (relative intensity) 294 (M^+, 1) 252 (22), 209 (11), 192 (32), 174 (30), 149 (34). Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.33; H, 7.26.

Preparations of Enediones 11. Mixtures of **6a–d** and **7a–d** were treated with pyridinium chlorochromate adsorbed on alumina in benzene as a solvent during 20 h according to the procedure as described by Cheng et al.[17] The workup and column chromatography on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (3:1) afforded the enediones **11a–d**.

4aβ-Methyl-3,4,4a,5-tetrahydronaphthalene-1(2*H*),7(6*H*)-dione (11a): yield 61.5%; compound **11a** had identical spectral characteristics with those reported in the literature.[45]

4β-Acetoxy-4aβ-methyl-3,4,4a,5-tetrahydronaphthalene-1(2*H*),7(6*H*)-dione (11b): yield 54%; mp 108–110 °C (from diisopropyl ether); ^{1}H NMR δ 1.30 (s, 3 H), 1.82–2.93 (m, 8 H), 2.13 (s, 3 H), 5.07 (dd, J = 7,9 Hz, 1 H), 6.28 (s, 1 H); mass spectrum, m/e (relative intensity) 236 (M^+, 3), 194 (100), 176 (12), 137 (61), 109 (19). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.15; H, 6.76.

4aβ,8-Dimethyl-3,4,4a,5-tetrahydronaphthalene-1(2*H*),7(6*H*)-dione (11c): yield 89%; mp 62–64 °C (from petroleum ether (bp 40–60 °C)/diisopropyl ether); ^{1}H NMR δ 1.20 (s, 3 H), 1.60–2.80 (m, 10 H), 1.78 (s, 3 H); mass spectrum, m/e (relative intensity) 192 (M^+, 100), 177 (61), 149 (25), 136 (22), 135 (15). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.67; H, 8.56.

4β-Acetoxy-4aβ,8-dimethyl-3,4,4a,5-tetrahydronaphthalene-1(2*H*),7(6*H*)-dione (11d): yield 83%; mp 118.5–120.5 °C (from diisopropyl ether); ^{1}H NMR δ 1.20 (s, 3 H), 1.65–2.80 (m, 8 H), 1.77 (s, 3 H), 2.08 (s, 3 H), 5.05 (dd, J = 5, 10 Hz, 1 H); mass spectrum, m/e (relative intensity) 250 (M^+, 23), 208 (100), 190 (14), 151 (31), 123 (26). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.42; H, 7.35.

Reduction of Enediones 11. (a) Titanium(III) Chloride (General Procedure). A solution of enedione **11** (1 mmol) in 15 mL of acetone was treated with 2–4 mL of a 15% titanium(III) chloride solution in aqueous 4% hydrogen chloride during 1–3 h at room temperature. The reaction mixture was poured into brine and extracted with dichloromethane (3 × 25 mL), and the combined organic layers were dried. Filtration and evaporation under reduced pressure afforded the crude dione mixtures. Column chromatography on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (5:1) gave the pure diones. Experimental details and yields are given in Table IV.

4aβ-Methyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1-(2*H*),7(8*H*)-dione (12a): ^{1}H NMR δ 1.01 (s, 3 H), 1.48–2.90 (m, 13 H); mass spectrum, m/e (relative intensity) 180 (M^+, 88), 151 (100), 137 (22), 123 (41); calcd for $C_{11}H_{16}O_2$ (M^+) m/e 180.1150, found m/e 180.1153.

4aβ-Methyl-3,4,4a,5,6,8aβ-hexahydronaphthalene-1-(2*H*),7(8*H*)-dione (14a). Compound **14a** had identical spectral characteristics with those reported in the literature.[3a]

4β-Acetoxy-4aβ-methyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione (12b): mp 139–141 °C (from diisopropyl ether); ^{1}H NMR δ 1.07 (s, 3 H), 1.35–2.90 (m, 11 H), 2.08 (s, 3 H), 5.15 (dd, J = 5, 10 Hz, 1 H); mass spectrum, m/e (relative intensity) 238 (M^+, 18), 194 (34), 178 (100), 149 (88). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.26; H, 7.33.

4β-Acetoxy-4aβ-methyl-3,4,4a,5,6,8aβ-hexahydronaphthalene-1(2*H*),7(8*H*)-dione (14b): mp 140–142 °C (from diisopropyl ether); ^{1}H NMR δ 1.30 (s, 3 H), 1.45–3.30 (m, 11 H), 2.19 (s, 3 H), 5.09 (t, J = 3 Hz, 1 H); mass spectrum, m/e (relative intensity) 238 (M^+, 10), 194 (100), 178 (50), 149 (59), 137 (46). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.24; H, 7.37.

4aβ,8α-Dimethyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1-(2*H*),7(8*H*)-dione (12c): mp 65–67 °C (from petroleum ether (bp 40–60 °C)); ^{1}H NMR δ 1.02 (d, J = 6 Hz, 3 H), 1.03 (s, 3 H), 1.42–2.97 (m, 12 H); ^{13}C NMR δ 12.77, 16.90, 23.54, 37.26, 39.72, 40.22, 40.44, 40.67, 41.89, 63.37, 209.74, 212.14; mass spectrum, m/e (relative intensity) 194 (M^+, 100), 165 (67), 151 (37), 137 (69), 123 (53), 111 (24). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.34; H, 9.30.

4aβ,8β-Dimethyl-3,4,4a,5,6,8aβ-hexahydronaphthalene-1-(2*H*),7(8*H*)-dione (13c): mp 78–80 °C (from petroleum ether (bp 40–60 °C)); ^{1}H NMR δ 0.88 (d, J = 6 Hz, 3 H), 0.98 (s, 3 H), 1.18–3.17 (m, 12 H); ^{13}C NMR δ 11.88, 22.03, 26.44, 29.79, 36.20, 37.10, 37.77, 40.16, 42.62, 66.44, 210.52, 210.97; mass spectrum, m/e (relative intensity) 194 (M^+, 99), 151 (51), 123 (100), 111 (45). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.45; H, 9.37.

4aβ,8α-Dimethyl-3,4,4a,5,6,8aβ-hexahydronaphthalene-1-(2*H*),7(8*H*)-dione (14c): mp 104–105 °C (from petroleum ether (bp 40–60 °C)/ether); ^{1}H NMR δ 1.09 (d, J = 7 Hz, 3 H), 1.38 (s, 3 H), 1.00–2.93 (m, 12 H); ^{13}C NMR δ 12.55, 23.65, 26.66, 30.85, 36.71, 38.66, 40.61, 41.56, 42.23, 63.31, 208.85, 211.64; mass spectrum m/e (relative intensity) 194 (M^+, 100), 179 (16), 165 (11), 151 (28), 149 (38), 137 (13), 124 (41), 111 (87). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.09; H, 9.36.

4β-Acetoxy-4aβ,8α-dimethyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione (12d). Titanium(III) chloride reduction of **11d** afforded a white solid.[46] ^{1}H NMR analysis indicated a 4:1 mixture of **12d** and **13d** [**13d**: ^{1}H NMR (major peaks) δ 0.90 (d, J = 6 Hz, 3 H), 1.02 (s, 3 H), 2.13 (s, 3 H), 5.90 (dd, J = 5, 10 Hz, 1 H)] which could not be separated by column chromatography. Recrystallization from ether/ethyl acetate gave pure **12d**: mp 140–142 °C; ^{1}H NMR δ 1.03 (d, J = 5 Hz, 3 H), 1.10 (s, 3 H), 1.38–3.10 (m, 10 H), 2.10 (s, 3 H), 5.08 (dd, J = 5, 11 Hz, 1 H); mass spectrum, m/e (relative intensity) 252 (M^+, 11), 192 (42). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.84; H, 8.12.

(b) Hydrogen Iodide (General Procedure). A solution of enedione **11** (1 mmol) in 15 mL of acetone was treated with 0.7–1.7 mL of a 57% aqueous hydrogen iodide solution during 2–7 h at room temperature. The reaction mixture was poured into saturated sodium bicarbonate, whereupon solid sodium thiosulfate was added. After decoloration the aqueous phase was extracted with dichloromethane (3 × 15 mL), and the combined organic layers were washed with brine and dried. Filtration and evaporation under reduced pressure afforded the crude dione mixtures.[46] Column chromatography on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (5:1) gave the pure diones.[47] Experimental details and yields are given in Table IV.

(c) Zinc Powder. A mixture of 0.512 g of **11d** (2.05 mmol) and 0.509 g of zinc powder (7.79 mmol) in 12.5 mL of acetic acid was refluxed for 4 h. The catalyst was removed by filtration and washed with ether (3 × 10 mL). Evaporation under reduced pressure afforded a yellow solid, which was dissolved in 25 mL of dichloromethane. The organic layer was washed with saturated sodium bicarbonate and brine, dried, and filtered. Evaporation of the filtrate under reduced pressure afforded 0.510 g of a yellow solid. Column chromatography on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (3:1) gave in the order of elution 0.413 g (80%) of a mixture of **12d** and **13d** in a ratio of 44:56 and 0.078 g (15%) of **14d**: mp 135–137 °C (from diisopropyl ether); ^{1}H NMR δ 1.13 (d, J = 7 Hz, 3 H), 1.32–3.05 (m, 9 H), 1.35 (s, 3 H), 2.18 (s, 3 H), 3.20 (m, 1 H), 4.83 (t, J = 2 Hz, 1 H); mass spectrum, m/e (relative intensity) 252 (M^+, 6), 210 (9), 192 (47), 163 (32). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.65; H, 8.12.

Acid Catalyzed Isomerization of 6a,b and 7a,b. To a solution of 3.446 g of a mixture of **6a** and **7a** (19.14 mmol) in 100 mL of ether was added 0.5 mL of concentrated hydrogen bromide. The mixture was stirred at room temperature for 1.5 h, and aqueous sodium bicarbonate was added. The ether layer was separated, and the water layer was extracted with ether (3 × 100 mL). The combined ethereal extracts were washed with brine

(45) Malhotra, S. K.; Hostynek, J. J.; Lundin, A. F. *J. Am. Chem. Soc.* **1968**, *90*, 6565.

(46) Under these conditions some hydrolysis of the acetate group occurred. Therefore, the crude reaction mixture was treated with a 2:1 mixture of pyridine and acetic anhydride.[5]

(47) Treatment of **11d** with hydrogen iodide afforded a 9:1 mixture of **12d** and **13d**. Recrystallization from petroleum ether (bp 40–60 °C)/ethyl acetate gave pure **12d** in a 71% yield.

and dried. Filtration and evaporation under reduced pressure gave an oil which was purified by column chromatography on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (6:1) and afforded 2.937 g (85%) of a 2:1 mixture of **12a** and **14a** according to ^{1}H NMR.

A mixture of **6b** and **7b** (5.00 mmol) was treated for 60 min as described above with a 4:1 mixture of ether and dichloromethane in place of pure ether. The workup and column chromatography gave 1.170 g (98%) of a 2:1 mixture of **12b** and **14b** according to ^{1}H NMR.

4aβ-Methyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione 7-Dimethyl Acetal (2a). To a stirred solution of 3.583 g of a mixture of **12a** and **14a** (19.9 mmol) in 100 mL of ether at room temperature were added 7.5 mL of trimethyl orthoformate and 0.100 g of *p*-toluenesulfonic acid monohydrate. The solution was stirred for 20 h, and then 1 mL of triethylamine was added. The reaction mixture was washed with brine and dried. After filtration and evaporation under reduced pressure, the residual oil was chromatographed on basic Woelm alumina (activity IV) with petroleum ether (bp 40–60 °C)/ethyl acetate (10:1) and afforded 3.238 g of (72%) of an inseparable mixture of **2a** and **16a** [**16a**: ^{1}H NMR (major peaks) δ 0.91 (s, 3 H), 3.12 (s, 3 H), 3.21 (s, 3 H)]. A solution of 0.904 g of this mixture (4.00 mmol) and 0.050 g of sodium in 20 mL of methanol was stirred for 20 h. The solvent was evaporated under reduced pressure, and the residue was taken up in 50 mL of dichloromethane. The organic layer was washed with brine and dried. Filtration and evaporation under reduced pressure afforded a brown oil which was chromatographed on basic Woelm alumina (activity IV) with petroleum ether (bp 40–60 °C)/ethyl acetate (10:1). According to ^{1}H NMR the resulting colorless oil (0.859 g) was pure **2a**: 0.859 g (yield 95%); ^{1}H NMR δ 0.80 (s, 3 H), 1.30–2.65 (m, 13 H), 3.12 (s, 3 H), 3.21 (s, 3 H); mass spectrum, *m/e* (relative intensity) 226 (M^+, 16), 195 (33), 101 (100). This material was sensitive to atmospheric moisture, and satisfactory analytical values could not be obtained.

4β-Hydroxy-4aβ-methyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione Dimethyl Acetal (2e). A mixture of **12b** and **14b** (6.95 mmol) was treated for 45 min as described above, using dichloromethane in place of ether. The workup and column chromatography gave 1.731 g (88%) of an inseparable mixture of **2b** [^{1}H NMR δ 0.87 (s, 3 H), 1.20–2.80 (m, 10 H), 2.09 (s, 3 H), 3.10 (s, 3 H), 3.21 (s, 3 H), 5.10 (dd, J = 5, 11 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 284 (M^+, 9), 252 (29), 177 (31), 101 (91)] and **16b** [^{1}H NMR δ 0.98 (s, 3 H), 1.20–2.75 (m, 10 H), 2.08 (s, 3 H), 3.12 (s, 3 H), 3.17 (s, 3 H), 5.55 (dd, J = 5, 11 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 284 (M^+, 3), 252 (28), 192 (20), 101 (100)]. A solution of 1.709 g of this mixture (6.02 mmol) and 0.081 g of sodium in 30 mL of methanol was stirred for 22 h. The solvent was evaporated under reduced pressure, and the residue was taken up in 100 mL of dichloromethane. The organic layer was washed with brine and dried. Filtration and evaporation under reduced pressure gave 1.383 g (95%) of a white solid which, according to ^{1}H NMR, was pure **2e**: mp 122–124 °C (from diisopropyl ether); ^{1}H NMR δ 0.80 (s, 3 H) 1.20–2.60 (m, 12 H), 3.12 (s, 3 H), 3.22 (s, 3 H), 3.82 (m, 1 H); mass spectrum, *m/e* (relative intensity) 242 (M^+, 20), 211 (29), 127 (32), 101 (100). Anal. Calcd for $C_{13}H_{22}O_4$: C, 66.44; H, 9.15. Found C, 64.37; H, 9.05.

4aβ,8α-Dimethyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione 7-Ethylene Acetal (1c). A mixture of 0.180 g of **12c** (0.93 mmol), 2.5 mL of 2-butanone dioxolane, and catalytic amounts of ethylene glycol and *p*-toluenesulfonic acid monohydrate was stirred for 3 h, and then 0.2 mL of triethylamine was added. The reaction mixture was taken up in 50 mL of ether, washed with brine, and dried. Filtration and evaporation under reduced pressure afforded 0.206 g (93%) of a white solid which, according to ^{1}H NMR, was pure **1c**: mp 73.5–75.5 °C (from petroleum ether (bp 40–60 °C)); ^{1}H NMR δ 0.81 (s, 3 H), 0.87 (d, J = 5 Hz, 3 H), 1.35–2.70 (m, 12 H), 3.93 (s, 4 H); mass spectrum, *m/e* (relative intensity) 238 (M^+), 99 (100). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.95; H, 9.66.

4aβ,8β-Dimethyl-3,4,4a,5,6,8aβ-hexahydronaphthalene-1(2*H*),7(8*H*)-dione 7-Ethylene Acetal (15c). A sample of **13c** (0.101 g, 0.52 mmol) was treated for 3 days as described above. The workup gave 0.111 g (90%) of a white solid which, according to ^{1}H NMR, was pure **15c**: mp 102–104 °C (from petroleum ether (bp 40–60 °C)); ^{1}H NMR δ 0.70 (d, J = 5 Hz, 3 H), 0.89 (s, 3 H), 1.25–2.60 (m, 12 H), 2.94 (s, 4 H); mass spectrum, *m/e* (relative intensity) 238 (M^+, 6), 99 (100). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.78; H, 9.34.

4β-Acetoxy-4aβ,8α-dimethyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione 7-Ethylene Acetal (1d). A sample of **12d** (1.079 g, 4.28 mmol) was treated for 24 h as described above. The workup gave 1.267 g (100%) of a white solid which, according to ^{1}H NMR, was pure **1d**: mp 112–114 °C (from diisopropyl ether); ^{1}H NMR δ 0.87 (d, J = 6 Hz, 3 H), 0.88 (s, 3 H), 1.35–2.75 (m, 10 H), 2.05 (s, 3 H), 3.93 (s, 4 H), 5.03 (dd, J = 5, 11 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 296 (M^+, 18), 99 (100). Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 64.95; H, 7.91.

4aβ-Methyl-8-methylene-3,4,4a,5,6,7,8,8aα-octahydronaphthalen-2(1*H*)-one (18a). The procedure of Corey et al. was employed. To a stirred solution of 50 mL of 0.36 M dimethylsulfinylsodium in dimethyl sulfoxide at room temperature was added 7.300 g of methyltriphenylphosphonium iodide (18.07 mmol). To the resulting mixture at room temperature was added dropwise a solution of 2.735 g of a mixture of **2a** and **16a** (12.10 mmol) in 20 mL of dimethyl sulfoxide. The reaction mixture was stirred for 20 h, poured into water (150 mL), and extracted with ethyl acetate (8 × 50 mL). The combined organic layers were washed with water (2 × 75 mL) and brine and dried. Filtration and evaporation under reduced pressure afforded crude **17a**: ^{1}H NMR δ 0.71 (s, 3 H), 1.00–2.45 (m, 13 H), 3.09 (s, 3 H), 3.18 (s, 3 H), 4.39 (br s, 1 H), 4.69 (br s, 1 H). A solution of **17a** in 25 mL of acetone, containing 1 mL of concentrated hydrogen chloride, was stirred for 15 min, poured into a mixture of saturated sodium bicarbonate (50 mL) and brine (50 mL), and extracted with ether (3 × 100 mL). The combined organic layers were dried, filtered, and evaporated under reduced pressure. The residual oil was chromatographed on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (6:1) and afforded 1.791 g (83%) of **18a**. The spectral characteristics of **18a** were identical with those reported in the literature.[3a]

5β-Hydroxy-4aβ-methyl-8-methylene-3,4,4a,5,6,7,8,8aα-octahydronaphthalen-2(1*H*)-one (18e). The procedure described above was employed by using 20.5 mL of 1 M dimethylsulfinylsodium, 8.274 g of methyltriphenylphosphonium iodide (20.48 mmol), and 2.253 g of **2e** (9.31 mmol) in 12.5 mL of dimethyl sulfoxide. The resulting product (2.100 g), eluted from basic alumina with petroleum ether (bp 40–60 °C)/ethyl acetate (2:1) and which was, according to ^{1}H NMR, crude **17e** [^{1}H NMR δ 0.71 (s, 3 H), 1.10–2.60 (m, 12 H), 3.13 (s, 3 H), 3.23 (s, 3 H), 3.45 (dd, J = 5, 12 Hz, 1 H), 4.49 (br s, 1 H), 4.77 (br s, 1 H)], was dissolved in mixture of 50 mL of acetone and 1 mL of concentrated hydrogen chloride and stirred at room temperature for 1.5 h. A small amount of solid sodium bicarbonate was added to neutralize the acid. The mixture was concentrated at room temperature under reduced pressure, and the residue was taken up in ether, washed with brine, dried, and filtered. Evaporation under reduced pressure afforded pure **18e**: 1.602 g (89%); mp 92–93 °C (from petroleum ether (bp 80–100 °C)); ^{1}H NMR δ 0.92 (s, 3 H), 1.35–2.60 (m, 12 H), 3.47 (dd, J = 5, 12 Hz, 1 H), 4.47 (br s, 1 H), 4.86 (br s, 1 H); mass spectrum, *m/e* (relative intensity) 194 (M^+, 19), 176 (57), 150 (31), 109 (42), 93 (100). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.03; H, 9.34.

Methyl 4aβ-Methyl-8-methylene-1,2,3,4,4a,5,6,7,8,8aα-decahydronaphthalene-2β-carboxylate (21a)[3a] and Methyl 4aβ-Methyl-8-methylene-1,2,3,4,4a,5,6,7,8,8aα-decahydronaphthalene-2α-carboxylate (22a). To a solution of 0.900 g of methoxy(phenylthio)(trimethylsilyl)methane[29] (4.00 mmol) in 20 mL of dry tetrahydrofuran was added dropwise at −80 °C 2.8 mL of a 15% solution of butyllithium in hexane. The mixture was stirred at −80 °C for 1 h, and then a solution of 0.538 g of **18a** (3.02 mmol) in 20 mL of dry tetrahydrofuran was added dropwise over a period of 10 min. This mixture was stirred at −80 °C for another hour, allowed to warm to room temperature, poured into water (100 mL), and extracted with ether (3 × 75 mL). The combined organic layers were washed with brine and dried. Filtration and evaporation under reduced pressure afforded a crude mixture of ketene *O,S*-acetals **20a**. A solution of **20a**, 0.35 mL of concentrated hydrogen chloride, and 1.00 g of mercury(II)

chloride in 100 mL of methanol was stirred at room temperature for 60 h, poured into water (100 mL) and extracted with ether (3 × 100 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated under reduced pressure. The residual oil was chromatographed on silica gel with petroleum ether (bp 40–60 °C)/ether (20:1) and afforded 0.553 g (82%) of a colorless oil, which according to GLC was an 1.2:1 mixture of **21a** and **22a**: ^{1}H NMR (major peaks) δ 0.74 (s, 3 H), 3.65 (s, 3 H). **21a**: mass spectrum, *m/e* (relative intensity) 222 (M^+, 49), 207 (36), 147 (100), 107 (98). **22a**: mass spectrum, *m/e* (relative intensity) 222 (M^+, 9), 207 (61), 147 (100), 107 (12). Treatment of this mixture with sodium methoxide in dry methanol at reflux temperature[48] under a nitrogen atmosphere for 60 h gave, according to GLC, a 7:1 mixture of **21a** and **22a**.

Methyl 5β-Hydroxy-4aβ-methyl-8-methylene-1,2,3,4,4a,5,6,7,8,8aα-decahydronaphthalene-2β-carboxylate (21e) and Methyl 5β-Hydroxy-4aβ-methyl-8-methylene-1,2,3,4,4a,5,6,7,8,8aα-decahydronaphthalene-2α-carboxylate (22e). A sample of **18e** (1.463 g, 7.54 mmol) was treated with 2.2 equiv of methoxy(phenylthio)(trimethylsilyl)methyllithium (**19**) as described above. The workup and column chromatography on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (9:1 to 2:1) gave 2.180 of **20e** (87%) as a mixture of two stereoisomers: mass spectrum, *m/e* (relative intensity) 330 (M^+, 100). A sample of this mixture (1.060 g, 3.21 mmol) was treated with 2.0 mL of 6 N hydrogen chloride and 0.875 g of mercury(II) chloride as described above. The workup and column chromatography on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (4:1 to 2:1) afforded 0.670 g (88%) of a colorless oil, which according to GLC was a 1.2:1 mixture of **21e** and **22e**: ^{1}H NMR (major peaks) δ 0.71 (s, 3 H) 3.70 (s, 3 H). **21e**: mass spectrum, *m/e* (relative intensity) 238 (M^+, 4) 220 (82), 194 (25), 161 (66), 135 (61), 119 (65), 93 (100). **22e**: mass spectrum, *m/e* (relative intensity) 238 (M^+, 0.3), 220 (44), 194 (46), 161 (28), 135 (75), 119 (33), 93 (100).

Methyl 4aβ-Methyl-8-methylene-5β-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,2,3,4,4a,5,6,7,8,8aα-decahydronaphthalene-2β-carboxylate (21g) and Methyl 4aβ-Methyl-8-methylene-5β-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,2,3,4,4a,5,6,7,8,8aα-decahydronaphthalene-2α-carboxylate (22g). The procedure of Grieco[36] et al. was employed. To a solution of 0.582 g of a mixture of **21e** and **22e** (2.45 mmol) and 0.123 g of pyridinium *p*-toluenesulfonate (0.49 mmol) in 17.5 mL of dry dichloromethane was added 0.45 mL of dihydropyran. The mixture was stirred at room temperature under a nitrogen atmosphere for 2 h, and 75 mL of ether was added. The organic solution was washed with brine and dried. Filtration and evaporation under reduced pressure gave 0.790 g (100%) of a colorless oil, which according to GLC was an 1.2:1 mixture of **21g** and **22g**: ^{1}H NMR (major peaks) δ 0.76 (s, 3 H), 3.70 (s, 3 H). **21g**: mass spectrum, *m/e* (relative intensity) 322 (M^+, 0.4), 221 (14), 85 (100). **22g**: mass spectrum, *m/e* (relative intensity) 322 (M^+, 0.1), 220 (15), 85 (100).

(±)-β-Eudesmol (23a). A sample of the equilibrated mixture of **21a** and **22a** (0.138 g, 0.62 mmol) was treated with 1.4 M ethereal methyllithium according to the procedure as described by Marshall.[3a] The workup and purification by column chromatography on silica gel with petroleum ether (bp 40–60 °C)/ether (15:1) afforded 0.118 g of **(±)-β-eudesmol 23a** (86%). The spectral characteristics of **23a** were identical with those reported in the literature.[3a]

A similar treatment of 0.133 g of the original 1.2:1 mixture of **21a** and **22a** (0.60 mmol) gave 0.070 g (53%) of (±)-β-eudesmol (**23**) and 0.054 g (41%) of its epimer **24a**. The spectral characteristics of the latter compound were identical with those reported in the literature.[32]

(±)-β-Selinene (25a). A solution of 0.176 g of an 1.2:1 mixture of **21a** and **22a** (0.79 mmol) and 1.900 g of salt-free methylenetriphenylphosphorane[33] (6.88 mmol) in dry tetrahydrofuran was refluxed under a nitrogen atmosphere for 84 h. The reaction mixture was allowed to come to room temperature, poured into water (100 mL), and extracted with petroleum ether (bp 40–60 °C, 4 × 75 mL). The combined organic layers were washed with brine and dried. Filtration and evaporation under reduced pressure gave an oil which was chromatographed on silica gel with petroleum ether (bp 40–60 °C). In order of elution 0.085 g of crude (±)-β-selinene (**25a**) and 0.066 g of a mixture of the starting materials **21a** and **22a** were isolated. Distillation of the first fraction gave 0.072 g (45%) of pure (±)-β-selinene (**25a**), bp 85 °C (bath temperature, 10 mm). The spectral characteristics of **25a** were identical with those of natural β-selinene.[34]

4aβ-Methyl-1-methylene-7β-isopropenyl-4β-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,2,3,4,4a,5,6,7,8,8aα-decahydronaphthalene (25g). To a mixture of 1.950 g of salt-free methylenetriphenylphosphorane[33] (7.07 mmol) and 0.428 g of methyltriphenylphosphonium bromide (1.20 mmol) in 15 mL of dry benzene was added at once a solution of 0.347 g of an 1.2:1 mixture of **21g** and **22g** (1.08 mmol) in 25 mL of dry benzene. The reaction mixture was stirred at reflux temperature under a nitrogen atmosphere for 5 h, allowed to come to room temperature, and filtered through a short column of basic alumina with the aid of petroleum ether (bp 40–60 °C)/ethyl acetate (10:1). The filtrate was evaporated under reduced pressure, and the residual oil was chromatographed on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (45:1), affording 0.264 g (80%) of a colorless oil, which was nearly pure **25g**: ^{1}H NMR δ 0.73 (s, 3 H), 1.05–2.50 (m, 18 H), 1.75 (s, 3 H), 3.28 (dd, *J* = 5, 12 Hz, 1 H), 3.43 (m, 1 H), 3.93 (m, 1 H), 4.49 (br s, 1 H), 4.63 (m, 1 H), 4.72 (br s, 3 H); mass spectrum, *m/e* (relative intensity) 304 (M^+, 1.7), 203 (13), 85 (100); calcd for $C_{20}H_{32}O_2$ (M^+) *m/e* 304.2402, found *m/e* 304.2401. Further elution with petroleum ether (bp 40–60 °C)/ethyl acetate (5:1) gave 0.021 g of a mixture of the starting materials **21g** and **22g**.

(±)-β-Dictyopterol (25e). The procedure of Grieco[36] et al. was employed. A solution of 0.123 g of **25g** (0.40 mmol) and 0.010 g of pyridinium *p*-toluenesulfonate (0.04 mmol) in 5 mL of ethanol was heated at 55 °C for 3 h. After evaporation under reduced pressure the residual oil was chromatographed on silica gel with petroleum ether (bp 40–60 °C)/ethyl acetate (10:1) and afforded 0.075 g (84%) of (±)-β-dictyopterol **25e** as a colorless oil which crystallized upon standing in a refrigerator: mp 71–73 °C; ^{1}H NMR δ 0.70 (s, 3 H), 1.00–2.50 (m, 13 H), 1.75 (br s, 3 H), 3.42 (dd, *J* = 5, 12 Hz, 1 H), 4.53 (br s, 1 H) 4.73 (br s, 3 H); mass spectrum, *m/e* (relative intensity) 220 (M^+, 28), 205 (28), 202 (42), 159 (60), 133 (59), 93 (100); calcd for $C_{15}H_{24}O$ (M^+) *m/e* 220.1827, found *m/e* 220.1828. The spectral characteristics of **25e** were identical with those reported in the literature.[9]

Acknowledgment. We thank Dr. M. A. Posthumus, Dr. C. A. Landheer, and C. J. Teunis for mass spectroscopic data, A. van Veldhuizen for recording NMR and ^{13}C NMR spectra, and H. Jongejan for carrying out the elemental analyses.

Registry No. (±)-**1c**, 61302-40-7; (±)-**1d**, 87262-03-1; (±)-**2a**, 87262-04-2; (±)-**2b**, 87262-43-9; (±)-**2e**, 87262-05-3; (±)-**3a**, 40573-28-2; (±)-**3b**, 32042-78-7; (±)-**3c**, 54832-12-1; (±)-**3d**, 87262-06-4; (±)-**4a**, 87262-07-5; (±)-**4b**, 17506-56-8; (±)-**4c**, 87262-08-6; (±)-**4d**, 87262-09-7; (±)-**5a**, 87262-10-0; (±)-**5b**, 87262-11-1; (±)-**5c**, 87262-12-2; (±)-**5d**, 87262-13-3; (±)-**6a**, 87262-14-4; (±)-**6b**, 87262-15-5; (±)-**6c**, 87262-16-6; (±)-**6d**, 87262-17-7; (±)-**7a**, 87281-33-2; (±)-**7b**, 87262-48-4; (±)-**7c**, 87262-19-9; (±)-**7d**, 87262-19-9; (±)-**8c**, 87262-20-2; (±)-**8d**, 87262-21-3; (±)-**9c**, 87262-22-4; (±)-**9d**, 87262-23-5; (±)-**10c** (β-epoxide), 87262-24-6; (±)-**10d** (β-epoxide), 87262-25-7; (±)-**11a**, 87332-35-2; (±)-**11b**, 87262-26-8; (±)-**11c**, 87262-27-9; (±)-**11d**, 87262-28-0; (±)-**12a**, 87332-36-3; (±)-**12b**, 87262-29-1; (±)-**12c**, 87262-30-4; (±)-**12d**, 87262-31-5; (±)-**13c**, 87262-33-7; (±)-**13d**, 87332-38-5; (±)-**14a**, 87332-37-4; (±)-**14b**, 87262-32-6; (±)-**14c**, 87262-34-8; (±)-**14d**, 87332-39-6; (±)-**15c**, 87332-40-9; (±)-**16a**, 87262-35-9; (±)-**16b**, 87262-47-3; (±)-**18d**, 87332-41-0; (±)-**18e**, 87262-36-0; **19**, 87262-37-1; (*E*)-(±)-**20a**, 87262-38-2; (*Z*)-(±)-**20a**, 87262-44-0; (*E*)-(±)-**20e**, 87262-45-1; (*Z*)-(±)-**20e**, 87262-46-2; (±)-**21a**, 87332-42-1; (±)-**21e**, 87262-39-3; (±)-**21g**, 87262-40-6; (±)-**22a**, 87333-66-2; (±)-**22e**, 87281-34-3; (±)-**22g**, 87262-41-7; (±)-**23a**, 3287-59-0; (±)-**25a**, 21488-94-8; (±)-**25e**, 87332-43-2; (±)-**25g**, 87262-42-8.

(48) Huffman, J. W.; Mole, M. L. *J. Org. Chem.* **1972**, *37*, 13.