with $F_0 > 4\sigma(F_0)$ were obtained by using the $\omega - 2\theta$ scanning method with a 2θ scan speed of 4°/min to 150°. The structure was solved by the RASA-II system (Rigaku Corp.) on the basis of the direct method (MULTAN)[27] and refined to a final R value of 0.091. The program was executed on a 16 bit/word minicomputer with a 64 Kbyte 1C memory and 10 Mbytes on magnetic disk. Further crystallographic details can be found in the supplemental material described in the paragraph at the end of this paper.

Registry No. 1, 84140-51-2; 2, 84140-50-1; 3, 32284-31-4; 4, 18395-45-4; 5a, 82959-04-4; 5b, 82959-05-5; 5c, 82959-06-6; 5d, 82959-07-7; 5e, 82959-08-8; 5f, 82959-09-9; 5g, 82959-10-2; 5h, 82959-11-3; 5i, 82959-12-4; 5j, 88704-56-7; 5k, 88704-57-8; 6a, 88764-10-7; 6b, 88704-65-8; 7, 42052-51-7; 9, 88764-11-8; 10, 88704-61-4; 11, 88704-62-5; 12, 88764-12-9; 13, 88704-63-6; 14a, 82959-14-6; 14b, 88704-64-7; 14c, 57548-41-1; 14d, 60669-64-9; 15a, 82959-15-7; 15b, 88704-58-9; 15c, 82959-16-8; 15d, 88704-59-0; 16b, 88764-08-3; 16c, 82978-52-7; 16d, 88764-09-4; 26, 88704-60-3; $C_6H_5COCH_3$, 98-86-2; p-$ClC_6H_4COCH_3$, 99-91-2; β-$C_{10}H_7COCH_3$, 93-08-3; p-$CH_3OC_6H_4COCH_3$, 100-06-1; p-$IC_6H_4COCH_3$, 13329-40-3; 2-$C_4H_3SCOCH_3$, 88-15-3; C_6H_5CHO, 100-52-7; p-ClC_6H_4CHO, 104-88-1; o-ClC_6H_4CHO, 89-98-5; acetone, 67-64-1; *trans*-4-phenyl-3-buten-2-one, 1896-62-4; 2-butanone, 78-93-3.

Supplementary Material Available: Tables of fractional atomic coordinates, bond lengths, and bond angles for 5f (3 pages). Ordering information is given on any current masthead page.

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Stereoselective Synthesis of (±)-3,4,4a,5,6,7,8,8a-Octahydronaphthalen-1(2*H*)-ones via Homogeneous Hydrogenation of (±)-5,6,7,8-Tetrahydronaphthalenones

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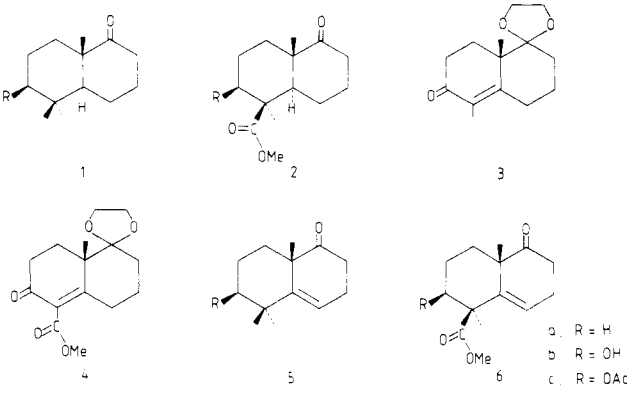
Homogeneous hydrogenation of 5,6,7,8-tetrahydronaphthalenone derivatives **7a,c** and **9b** using tris(triphenylphosphine)rhodium(I) chloride gave (±)-5,5,8aβ-trimethyl-3,4,4aα,5,6,7,8,8a-octahydronaphthalen-1(2*H*)-one (**1a**) and (±)-methyl 1-oxo-5α,8aβ-dimethyl-6β-hydroxy-1,2,3,4,4aα,5,6,7,8,8a-decahydronaphthalene-5β-carboxylate (**2b**) in good yields.

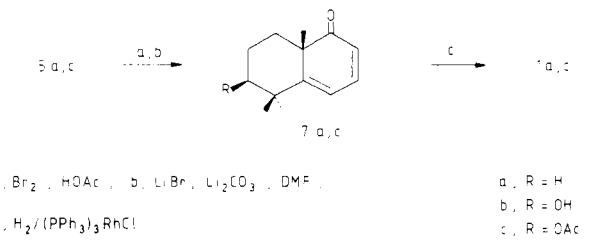
In connection with several planned terpene syntheses in our laboratory, convenient stereocontroled preparations of the trans-fused bicyclic ketones **1** and **2** were required. The obvious procedures for the preparation of these compounds, i.e., reductive alkylation of **3** and **4** or catalytic hydrogenation of **5** and **6**, respectively, turned out to be unattractive. Reductive alkylation of **3** gave good results in small-scale preparations,[1] but on a larger scale mixtures of reduced and alkylated products were obtained that required extensive purification. Reductive alkylation of **4** seemed not very promising since dissolving metal reduction of **4** gives mixtures of cis- and trans-fused reduction products[2] and methylation of the trans-fused enolate affords a methylated product with the epimeric configuration at C-5.[3] The reductive elimination developed by Coates et al.[4] and applied in the total synthesis of LLZ-1271α[5] has the disadvantage that no functionality remains in ring A, and this method is therefore unsuitable for the preparation of **2b** and **2c** (Chart I).

The catalytic hydrogenation of **5** is reported but proved to be rather irreproducible.[1b,6] Catalytic hydrogenation of **6** was unsuccessful, and moderate results were obtained when compounds related to **6** were reduced.[7]

Chart I



Scheme I



In this paper a synthesis of racemic **1** and **2** is described by using compounds **7** and **9** as key intermediates. Extension of the unsaturated system in ring B in **5** or **6** followed by homogeneous catalytic hydrogenation with

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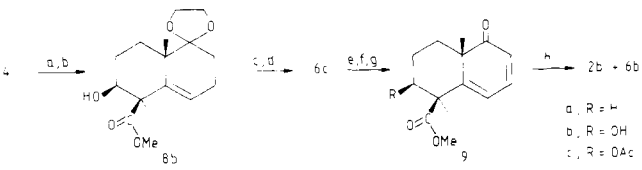
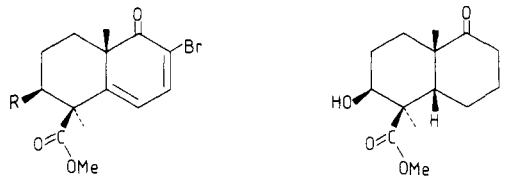
0022-3263/84/1949-1110$01.50/0

Scheme II



a, KO*t*Bu, H_3Cl b, $NaBH_4$, c, $H^{\oplus}$, H_2O, d, Ac_2O, pyr, e, Br_2, HOAc
f, Δ Br, Li_2CO_3, DMF, g, K_2CO_3, H_2O, h, $H_2/(PPh_3)_3RhCl$

Chart II



10 a, R = OH
b, R = OAc

11

tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst) proved to be a useful method for the stereoselective reduction of the diene system. Via this detour a stereoselective reduction of the 4–4a double bond in **5** and **6** can be achieved.

Starting from ketones **5a**[8] and **5c**,[8] the dienones **7a** and **7c** were prepared as described in Scheme I.[9] When these compounds were hydrogenated with Wilkinson's catalyst at 28 psi, the desired trans-fused bicyclic ketones **1a** and **1c** were isolated in about 80% yield. Small quantities (<5%) of partly hydrogenated products were formed, and no cis-fused reduction products could be detected. Hydrogenation of **5c** with Pd/C gave 1:1 mixtures of cis- and trans-fused reduction products. The stereochemistry of **1a** and **1c** was proved by comparison of the spectra with those of samples prepared following literature procedures.[1b,6]

The dienone **9b** was prepared as shown in Scheme II. The bromination–dehydrobromination procedure gave the best results when applied to the acetate **6c**. Small quantities (<10%) of the unsaturated bromide **10** (vide infra) were isolated also.

When keto ester **9b** was hydrogenated under the conditions used for **7a** and **7c** (28 psi hydrogen pressure), the products obtained were the desired trans-fused keto ester **2b** and the unsaturated keto ester **6b** in a 1:2 ratio.

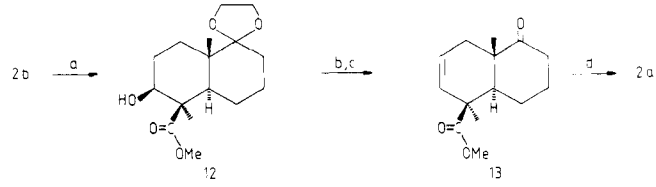
A reduction at higher pressure (150 psi) was performed to minimize the formation of **6b**, and indeed the amount of **6b** decreased apreciably, but now the formation of the cis-fused keto ester **11** became a side reaction (Chart II). Obviously the hydrogen pressure influences the regio- and stereochemistry of the reduction, and therefore a series of hydrogenation was carried out at increasing hydrogen pressure (see Table I). The optimum hydrogen pressure turned out to be about 60 psi. Later on we found that when the solution of the substrate and catalyst was stirred in contact with air for 1 h before the hydrogenation was started, a complete conversion of the dienones **9b** or **9c** into the trans-fused keto esters **2b** or **2c** could be achieved. The stereochemistry of the trans-fused keto ester **2b** was proved by spectroscopy and by conversion of **2b** into the known **2a**[5] following the route outlined in Scheme III. Protection of the keto group in **2b** proved necessary to

Table I. Hydrogenation of Dienone 9b with $RhCl(Ph_3P)_3$ (Method A)

entry	pressure, psi	2b	6b	11
1	24	37	63	
2[a]	44	62	38	
3	55	80	20	
4	60	87	13	
5	70	±73	±27	<10
6	150	70	20	10
7	230	30	40	30

[a] In this run the acetate **9c** was hydrogenated. The acetate group became partially hydrogenated to the hydroxyl group, so in the other runs the hydroxy dienone **9b** was hydrogenated.

Scheme III



a, MED, H^+, b, $POCl_3$, pyr, c, H^+, H_2O, d, H_2, Pd/C

avoid the formation of chlorinated products during the dehydration.

An attempt to hydrogenate **6b** directly using Wilkinson's catalyst, even at 1200 psi hydrogen pressure, was unsuccessful, and also the bromo dienone **10** could not be hydrogenated. These two examples again illustrate the fact that triply substituted olefines are generally not hydrogenated with Wilkinson's catalyst.[10] In some situations this type of olefin can be "activated" by the presence of a second conjugated double bond.[10] In our case extension of the unsaturated system in **5** and **6** to a dienone system in **7** and **9** clearly enhances the reducibility in homogeneous hydrogenations. Both double bonds can be reduced, but the greater steric hindrance in keto ester **9b** becomes evident from the isolation of **6b** in reasonable amounts. In the hydrogenation of **7a** only traces of **5a** were found. The α,β-unsaturated ketone was isolated as a byproduct when low catalyst concentrations were used. The formation of cis-fused reduction products can be avoided. Especially when larger quantities of **1** are required, this reduction procedure offers a good alternative for the existing methods. In the case of keto esters **2** this route paves the way to the synthesis of ring-A-functionalized podolactones.[11]

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were determined on a Varian EM-390 or a Hitachi-Perkin-Elmer R-24B spectrometer. The line positions for the ^1H NMR spectra are given in the δ scale as parts per milion downfield from internal tetramethylsilane. Mass spectral data and exact mass measurements were obtained with a VG MM 70–70 or an AEI-MS-902 instrument.

5,5,8aβ-Trimethyl-5,6,7,8-tetrahydronaphthalen-1(8a*H*)-one (7a). To a solution of 7.44 g (38.7 mmol) of ketone **5a**[8] in 100 mL of glacial acetic acid was added dropwise a solution of 6.19 g (38.7 mmol) of bromine in 31.9 mL of glacial acetic acid at room temperature under nitrogen. After 30 min the solution

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was poured into ice water (200 mL), and the aqueous layer was extracted with ether (3 × 100 mL). The organic layer was washed with water (75 mL), saturated aqueous sodium bicarbonate solution (75 mL), and brine and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave the crude bromide. The crude α-bromo ketone was dissolved in 100 mL of dimethylformamide, and then 5.1 g (59 mmol) of lithium bromide and 6.8 g (91 mmol) of lithium carbonate were added. The suspension was stirred in a preheated oil bath (120 °C) for 30 min under N_2, cooled, poured into 150 mL of water, and extracted with ether (3 × 150 mL). The organic layer was washed with water (75 mL) and brine, and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure yielded a light yellow solid, which was chromatographed over SiO_2 (150 g, eluent ether–petroleum ether (40–60 °C), 1:9). The dienone **7a** was isolated in an 80% yield as a light yellow solid: ^1H NMR ($CDCl_3$) δ 1.19 (s, 3 H), 1.26 (s, 3 H), 1.38 (s, 3 H), 1.1–2.5 (m, 6 H), 5.89 (d, J = 10 Hz, 1 H), 6.17 (d, J = 7 Hz, 1 H), 6.98 (dd, J = 7, 10 Hz, 1 H); mass spectrum (70 eV), m/e (relative intensity) 190 (100, M^+), 175 (58), 147 (73), 134 (56), 122 (75), 121 (75), 91 (76), 69 (56), 41 (73); calcd for $C_{13}H_{18}O$ M^+ 190.1358, found M^+ 190.1357.

6β-Acetoxy-5,5,8aβ-trimethyl-5,6,7,8-tetrahydronaphthalen-1(8a*H*)-one (7c). The procedure described for the synthesis of dienone **7a** was employed. The crude dienone **7c** (260 mg, 1.05 mmol) was chromatographed over SiO_2 (50 g, eluent ether–petroleum ether (40–60 °C), 1:1). The first material eluted was identified as 6β-acetoxy-2-bromo-5,5,8aβ-trimethyl-5,6,7,8-tetrahydronaphthalen-1(8a*H*)-one, a light yellow solid (31 mg, 9.5%): mp 183.0–184.0 °C; ^1H NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.26 (s, 3 H), 1.43 (s, 3 H), 1.3–2.3 (m, 4 H), 2.08 (s, 3 H), 4.54 (dd, J = 6, 8 Hz, 1 H), 6.11 (d, J = 7 Hz, 1 H), 7.42 (d, J = 7 Hz, 1 H); mass spectrum (70 eV), m/e (relative intensity) 328, 326 (4.5 M^+), 268, 266 (26, 28), 229, 227 (80, 86), 187 (40), 172 (34), 43 (100). Anal. Calcd for $C_{15}H_{19}BrO_3$: C, 55.06; H, 5.85. Found: C, 55.24; H, 5.88. The second material eluted was identified as dienone **7c** (196 mg, 79%), a light yellow solid: mp 115.5–116.0 °C; ^1H NMR ($CDCl_3$) δ 1.18 (s, 3 H), 1.28 (s, 3 H), 1.39 (s, 3 H), 1.1–2.3 (m, 4 H), 2.07 (s, 3 H), 4.55 (dd, J = 7, 8 Hz, 1 H), 5.94 (d, J = 10 Hz, 1 H), 6.25 (d, J = 7 Hz, 1 H), 7.02 (dd, J = 7, 10 Hz, 1 H); mass spectrum (70 eV), m/e (relative intensity) 248 (14, M^+), 206 (20), 188 (55), 173 (64), 149 (100), 145 (72), 43 (33). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.62; H, 8.34.

5,5,8aβ-Trimethyl-3,4,4aα,5,6,7,8,8a-octahydronaphthalen-1(2*H*)-one (1a). To a solution of 6.0 g (31 mmol) of ketone **7a** in 210 mL of a mixture of 1:1 absolute methanol–dry benzene was added 850 mg (0.93 mmol) of Wilkinson's catalyst (3 mol %). This mixture was hydrogenated in a hydrogen atmosphere at a pressure of 28 psi. Column chromatography over SiO_2 (150 g, eluent ether–petroleum ether (40–60 °C), 1:9) yielded 4.81 g (80%) of ketone **1a**: ^1H NMR ($CDCl_3$) δ 0.91 (s, 3 H), 0.95 (s, 3 H), 1.16 (s, 3 H), 1.0–2.9 (m, 13 H). The additional characteristics were identical with those reported in the literature.[1b]

6β-Acetoxy-5,5,8aβ-trimethyl-3,4,4aα,5,6,7,8a-octahydronaphthalen-1(2*H*)-one (1c). The hydrogenation of 1.0 g (4 mmol) of ketone **7c** was performed as outlined above at a pressure of 28 psi. The acetate **1c** was obtained in 80% yield (0.81 g): ^1H NMR ($CDCl_3$) δ 0.90 (s, 3 H), 0.97 (s, 3 H), 1.18 (s, 3 H), 1.1–2.8 (m, 11 H), 2.05 (s, 3 H), 4.45 (dd, J = 6, 11 Hz, 1 H). The additional characteristics were identical with those reported in the literature.[6]

Methyl 1,1-(Ethylenedioxy)-6-oxo-8aβ-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene-5-carboxylate (4). The procedure of Ellis, Dutcher, and Heathcock[12] was employed for the synthesis of the diketo ester by using 23.9 g (149 mmol) methyl 5-methoxy-3-oxopentanoate[13] and 20.7 g (164 mmol) 2-methylcyclohexane-1,3-dione.[14] A yield of 27.0 g (82%) of the product was obtained: mp 69–70 °C (lit.[7] mp 70–71 °C); ^1H NMR ($CDCl_3$) δ 1.48 (s, 3 H), 1.6–2.8 (m, 10 H), 3.78 (s, 3 H). The procedure of Bauduin and Pietrasanta[15] was employed for the protection of the carbonyl function at C-1. A total of 20.6 g (87.1 mmol) of diketo ester was dissolved in 75 mL of 2-methyl-2-ethyl-1,3-dioxolane.[15] Glycol (1.5 mL) and 200 mg of *p*-toluenesulfonic acid were added, and the mixture was stirred at room temperature for 4 days. TLC examination revealed that the reaction was complete. The reaction mixture was poured into 150 L of a saturated sodium bicarbonate solution and extracted with ether (3 × 150 mL). The combined organic layers were washed with water (100 mL) and brine and then dried (Na_2SO_4). The solvent was evaporated, and the residual light yellow oil was crystallized from diisopropyl ether–methanol to give 15.8 g of keto ester acetal **4**. The mother liquor was chromatographed over SiO_2 (100 g). Elution with 3:1 ether–petroleum ether (40–60 °C) gave an additional 4.2 g of product. The total yield was 82%: mp 121–122 °C (lit.[7] mp 120–122 °C); ^1H NMR ($CDCl_3$) δ 1.38 (s, 3 H), 1.8–2.7 (m, 10 H), 3.76 (s, 3 H), 3.93 (s, 4 H).

Methyl 1,1-(Ethylenedioxy)-5α,8aβ-dimethyl-6β-hydroxy-1,2,3,5,6,7,8,8a-octahydronaphthalene-5β-carboxylate (8b). For the methylation of ketone **4**, the procedure of Mangoni et al.[16] was addapted. A solution of 9.09 g (32.4 mmol) of keto ester ketal **4** in 50 mL of 1:1 of dry benzene and *tert*-butyl alcohol was added dropwise in 30 min to a stirred solution of 4.10 g (33.5 mmol) of commercial potassium *tert*-butoxide in 500 mL of 4:1 dry benzene–*tert*-butyl alcohol under N_2. After being stirred for 15 min at 40 °C, the dark red solution was cooled to 0 °C in an ice bath. Then 25 mL of methyl iodide was added and the mixture refluxed for 17 h. The cooled reaction mixture was poured into water and the layers were separated. The aqueous layer was extracted with ether (2 × 150 mL). The combined organic layer washed with water (100 mL) and brine and dried (Na_2SO_4). The solvent was evaporated under reduced pressure, and the residual white solid was crystallized from diisopropyl ether–methanol to give 7.15 g of methylated keto ester ketal. The mother liquor was chromatographed over SiO_2 (50 g, eluent ether–petroleum ether (40–60 °C), 3:1) to afford an additional 1.06 g. A total yield of 8.12 g (86%) was obtained: mp 120–121 °C (lit.[7] mp 121.5–122.5 °C); ^1H NMR ($CDCl_3$) δ 1.25 (s, 3 H), 1.49 (s, 3 H), 1.7–2.8 (m, 8 H), 3.69 (s, 3 H), 4.0 (br s, 4 H), 5.59 (dd, J = 4, 4 Hz, 1 H).

For the reduction of the carbonyl function at C-6, the procedure of Pelletier, Chappell, and Prabhakar[7] was used, affording hydroxy ester ketal **8b** as a solid material (90% yield). NMR analyses showed a single compound, which was used without further purification in the next step: ^1H NMR ($CDCl_3$) δ 1.07 (s, 3 H), 1.51 (s, 3 H), 1.4–2.4 (m, 8 H), 3.13 (dd, J = 6, 9 Hz, 1 H), 3.55 (br s, 1 H, exchanges with D_2O), 3.61 (s, 3 H), 3.92 (s, 4 H), 5.79 (dd, J = 4, 4 Hz, 1 H).

Methyl 1-Oxo-6β-acetoxy-5α,8aβ-dimethyl-1,5,6,7,8,8a-hexahydronaphthalene-5β-carboxylate (9c). Compound **8b** was converted into acetate **6c** according to Pelletier et al.[7] The bromination and dehydrobromination of acetate **6c** was performed as described for the synthesis of compound **7a**. There was used 7.34 g (25.0) of acetate **6c** and the crude product was chromatographed over SiO_2 (150 g, eluent ether–petroleum ether (40–60 °C), 2:3). The first compound isolated was 0.36 g (4%) of bromo acetate **10b**, which was not further characterized but hydrolyzed to bromo hydroxy ketone **10a**. The second compound eluted was identified as dienone acetate **9c** (6.61 g, 91%): mp 108.0–108.5 °C; ^1H NMR ($CDCl_3$) δ 1.21 (s, 3 H), 1.47 (s, 3 H), 1.3–2.8 (m, 4 H), 2.00 (s, 3 H), 3.66 (s, 3 H), 4.52 (dd, J = 4, 12 Hz, 1 H), 6.03 (d, J = 10 Hz, 1 H), 6.41 (d, J = 7 Hz, 1 H), 7.10 (dd, J = 7, 10 Hz, 1 H); mass spectrum (70 eV), m/e (relative intensity) 292 (12, M^+), 232 (32), 173 (100), 172 (41), 145 (87), 43 (93). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.70; H, 6.95.

Methyl 1-Oxo-5α,8aβ-dimethyl-6β-hydroxy-1,5,6,7,8,8a-hexahydronaphthalene-5β-carboxylate (9b). To a solution of 6.28 g (21.5 mmol) of acetate **9c** in 100 mL of methanol was added at 0 °C a solution of 2.09 g (14.5 mmol) of potassium carbonate. After being stirred for 4 h, the mixture was poured into ice water, and the aqueous layer extracted with dichloromethane (5 × 60 mL). The combined organic layers were washed with water (100 mL) and brine and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure yielded a light yellow solid, which was crystallized from diisopropyl ether to afford 4.69 g (18.8

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(16) Mangoni, L.; Adinolfi, M.; Laonigro, G.; Caputo, R. *Tetrahedron* **1972**, *28*, 611.

mmol, 87%) of hydroxy dienone **9b**: mp 125.0–126.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 3 H), 1.62 (s, 3 H), 1.3–2.4 (m, 4 H), 3.14 (dd, J = 6, 11 Hz, 1 H), 3.62 (s, 3 H), 3.72 (br s, 1 H, exchanges with D_2O), 5.99 (d, J = 10 Hz, 1 H), 6.34 (d, J = 6 Hz, 1 H), 7.05 (dd, J = 6, 10 Hz, 1 H); mass spectrum (70 eV), m/e (relative intensity) 250 (20, M^+), 232 (5), 218 (36), 194 (87), 173 (41), 162 (100), 161 (34), 145 (49), 133 (36). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.98; H, 7.23.

Methyl 1-Oxo-2-bromo-5α,8aβ-dimethyl-6β-hydroxy-1,5,6,7,8,8a-hexahydronaphthalene-5β-carboxylate (10a). Bromo dienone acetate **10b** was treated as is described for the synthesis of compound **9b** from **9c**. This afforded 300 mg (0.9 mmol, 86%) of bromo dienone **10a**: mp 154.5–155.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 3 H), 1.64 (s, 3 H), 1.3–2.5 (m, 4 H), 3.18 (dd, J = 5, 9 Hz, 1 H), 3.68 (s, 3 H), 3.70 (br s, 1 H, exchanges with D_2O), 6.31 (d, J = 7 Hz, 1 H), 7.59 (d, J = 7 Hz, 1 H); mass spectrum (70 eV), m/e (relative intensity) 330, 328 (19, 21, M^+), 298, 296 (35, 37), 274, 272 (94, 100), 273, 271 (42, 40), 242, 240 (93, 90), 241, 239 (50, 44), 213, 211 (50, 42), 192 (32), 172 (56), 43 (68). Anal. Calcd for $C_{14}H_{17}BrO_4$: C, 51.08; H, 5.21. Found: C, 51.36; H, 5.06.

General Procedures for the Hydrogenation of the Dienones 9b and 9c with Tris(triphenylphosphine)rhodium(I) Chloride. Method A. To a solution of 4 mmol of dienone in 40 mL of absolute methanol and dry benzene (1:1) was added 200 mg of Wilkinson's catalyst (5 mol %). This mixture was hydrogenated in a hydrogen atmosphere at the indicated pressure (see Table I). The yields obtained after column chromatography over SiO_2 were approximately 80%.

Method B. To a solution of 4 mmol of the dienone in 40 mL of absolute methanol and dry benzene (1:1) was added 200 mg of Wilkinson's catalyst (5 mol %). When the catalyst was dissolved the solution was stirred in contact with air for 1 h. The mixture was hydrogenated at a hydrogen pressure of 130 psi. Column chromatography over SiO_2 afforded 80% of hydroxy keto ester **2b**.

Methyl 1-Oxo-6β-acetoxy-5α,8aβ-dimethyl-1,2,3,4,4aα,5,6,7,8,8a-decahydronaphthalene-5β-carboxylate (2c). The procedure outlined above was used (see Table I): mp 127.5–128.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 3 H), 1.27 (s, 3 H), 1.0–2.8 (m, 11 H), 2.06 (s, 3 H), 3.72 (s, 3 H), 4.53 (dd, J = 5, 13 Hz, 1 H); mass spectrum (70 eV), m/e (relative intensity) 268 (3, M^+), 236 (52), 226 (15), 209 (16), 208 (100), 193 (11). Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 64.94; H, 8.26.

Methyl 1-Oxo-5α,8aβ-dimethyl-6β-hydroxy-1,2,3,4,4aα,5,6,7,8,8a-decahydronaphthalene-5β-carboxylate (2b). The procedure outlined above was used (see Table I): mp 158.0–159.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 3 H), 1.40 (s, 3 H), 1.0–2.6 (m, 11 H), 3.08 (dd, J = 6, 9 Hz, 1 H), 3.6 (br s, 1 H, exchanges with D_2O), 3.73 (s, 3 H); mass spectrum (70 eV), m/e (relative intensity) 254 (6, M^+), 236 (30), 222 (22), 204 (18), 165 (46), 149 (24), 125 (60), 121 (34), 107 (45), 95 (100). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.35; H, 8.80.

Methyl 1-Oxo-5α,8aβ-dimethyl-6β-hydroxy-1,2,3,4,4aβ,5,6,7,8,8a-decahydronaphthalene-5β-carboxylate (11). A side product of the hydrogenation of **9b** at higher pressure (see Table I): mp 105.5–107.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 3 H), 1.34 (s, 3 H), 1.2–2.7 (m, 11 H), 3.60 (br s, 1 H, exchanges with D_2O), 3.68 (dd, J = 5, 9 Hz, 1 H), 3.70 (s, 3 H); mass spectrum (70 eV), m/e (relative intensity) 254 (4, M^+), 236 (38), 222 (16), 204 (38), 165 (38), 149 (40), 121 (42), 107 (56), 95 (100). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.26; H, 8.81.

Methyl 1,1-(Ethylenedioxy)-5α,8aβ-dimethyl-6β-hydroxy-1,2,3,4,4aα,5,6,7,8,8a-decahydronaphthalene-5β-carboxylate (12). For the protection of the carbonyl function at C-1, the procedure described for the synthesis of acetal **4** was employed to give 252 mg (0.85 mmol, 80%) of hydroxy acetal **12**: ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 1.36 (s, 3 H), 1.1–2.3 (m, 11 H), 3.11 (dd, J = 4, 10 Hz, 1 H), 3.15 (br s, exchanges with D_2O, 1 H), 3.67 (s, 3 H), 3.90 (br s, 4 H); mass spectrum (70 eV), m/e (relative intensity) 298 (18, M^+), 99 (100), 86 (24); calcd for $C_{16}H_{26}O_5$ M^+ 298.1780, found M^+ 298.1790.

Methyl 1-Oxo-5α,8aβ-dimethyl-1,2,3,4,4aα,5,8,8a-octahydronaphthalene-5β-carboxylate (13). To an ice-cooled solution of 252 mg (0.85 mmol) of hydroxy acetal **12** in 10 mL of dry pyridine was added at 0 °C 0.5 mL of phosphorus oxytrichloride, and then the solution was refluxed for 1 h. The cooled reaction mixture was poured into ice water and extracted with dichloromethane (4 × 50 mL). The combined organic layers were washed with 1 N hydrochloric acid (50 mL), saturated sodium bicarbonate solution (50 mL), and brine and dried (Na_2SO_4). The solution was concentrated in vacuo, and the residual oil (112 mg) was dissolved in 5 mL of methanol. Then 0.5 mL of 4 N hydrochloric acid was added, and the reaction mixture was stirred for 17 h. The reaction mixture was poured into ice water containing 5 mL of saturated sodium bicarbonate solution, and this aqueous layer was extracted with dichloromethane (4 × 50 mL). The organic layers were washed with brine and dried (Na_2SO_4). The crude product that was obtained after evaporation of the solvent was chromatographed over SiO_2 (30 g, eluent ether–petroleum ether (40–60 °C), 1:1) and yielded 84 mg (0.36 mmol, 42%) of **13**: ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 3 H), 1.30 (s, 3 H), 1.1–2.6 (m, 8 H), 3.65 (s, 3 H), 5.60 (m, 2 H); mass spectrum (70 eV), m/e (relative intensity) 236 (26, M^+), 193 (56), 177 (38), 159 (100), 133 (41), 85 (50); calcd for $C_{14}H_{20}O_3$ M^+ 236.1412, found M^+ 236.1420.

Methyl 1-Oxo-5α,8aβ-dimethyl-1,2,3,4,4aα,5,6,7,8,8a-decahydronaphthalene-5β-carboxylate (2a). To a solution of 70 mg (0.29 mmol) of enone **13** was added 50 mg of palladium on charcoal, and this mixture was hydrogenated at atmospheric pressure for 5 h. The catalyst was filtered off and the solution concentrated in vacuo. The crude product (67 mg, 95%) was crystallized from petroleum ether (40–60 °C) to give 30 mg of **2a**: mp 85–87 °C (lit.[5] mp 87.5–88.5 °C); ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 3 H), 1.20 (s, 3 H), 1.1–2.8 (m, 13 H), 3.68 (s, 3 H); mass spectrum (70 eV), m/e (relative intensity) 238 (4, M^+) 210 (27), 151 (31), 110 (22), 109 (100), 101 (21), 95 (26), 81 (23); calcd for $C_{14}H_{22}O_3$ M^+ 238.1569, found M^+ 238.1550. These data are in agreement with those reported in the literature.[5]

Registry No. **1a**, 65556-24-3; **1c**, 88852-61-3; **2a**, 15292-89-4; **2b**, 88825-31-4; **2c**, 88802-20-4; **4**, 10208-23-8; **4** diketo derivative, 10208-22-7; **5a**, 88852-62-4; **5a** bromo derivative, 88802-21-5; **5c**, 88852-63-5; **6c**, 20380-41-0; **7a**, 88802-22-6; **7c**, 88802-23-7; **8b**, 10208-25-0; **8b** keto derivative, 10208-24-9; **9b**, 88802-24-8; **9c**, 88825-09-6; **10a**, 88802-25-9; **10b**, 88802-26-0; **11**, 88802-27-1; **12**, 10208-26-1; **13**, 88802-28-2; **13** acetal derivative, 88802-29-3; (±)-6β-acetoxy-2-bromo-5,5,8aβ-trimethyl-5,6,7,8-tetrahydronaphthalen-1(8a*H*)-one, 88802-30-6; methyl 5-methoxy-3-oxopentanoate, 62462-05-9; 2-methylcyclohexane-1,3-dione, 1193-55-1; tris(triphenylphosphine)rhodium(I) chloride, 14694-95-2.