Synthesis of Vicinal Stereogenic Tertiary and Quaternary Centers Using Chiral Bicyclic Lactams and Diastereoselective Protonation. Asymmetric Synthesis of (+)-Laurene

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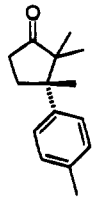
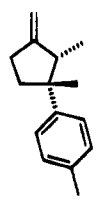
The chiral bicyclic lactam **5**, previously reported in the synthesis of (−)-α-cuparenone, was used to construct the more complex title compound **2**. A mixture of cyclopentenones **8** and **9** was subjected to deprotonation/reprotonation to provide **8** in high diastereomeric excess. Transformation of **8** to the title compound was achieved by catalytic hydrogenation to **13**, followed by methylenation with the Tebbe reagent.

We have previously demonstrated that chiral, nonracemic bicyclic lactams are useful precursors to enantiomerically pure 4,4-dialkylcyclopentenones.[1] This chemistry led to the synthesis of naturally occurring (−)-α-cuparenone (**1**) bearing a single stereogenic quaternary center.[2] However, we felt that (+)-laurene (**2**), containing two contiguous asymmetric centers, would serve as a more complex and challenging application of this methodology. Although several racemic syntheses of this natural product have been performed, only one enantioselective approach has been described[3] which produced laurene in only 71% optical purity on the basis of literature rotation. We now report an asymmetric route to (+)-laurene (**2**) which furnishes the natural enantiomer in >96% ee and an overall yield of 10%.



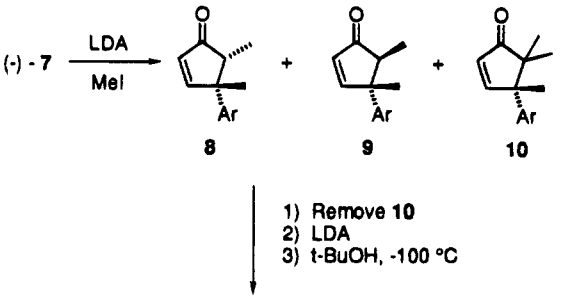
(+) - 1



(+) - 2

This present synthesis is based on our previous observation of predominant *endo*-alkylation of lactams **3** (Scheme 1).[2] Thus, condensation of racemic keto acid **4** with (*R*)-valinol gave the α-aryl bicyclic lactam **3** as a mixture of diastereomers. Alkylation of the enolate derived from **3** with methyl iodide gave **5** as the result of predominant approach of the electrophile from the *endo* face. Recrystallization of the crude product gave (+)-**5** as a single diastereomer in 64% yield. Using the synthetic sequence described earlier,[2] partial reduction, hydrolysis, and intramolecular aldol cyclization of the intermediate keto aldehyde **6** provided the requisite cyclopentenone (−)-**7** in 80% overall yield from (+)-**5**. The scheme to reach laurene **2** now would involve (a) stereoselective monomethylation α to the carbonyl group, (b) reduction of the C=C, and (c) olefination of the carbonyl without affecting the α-methyl group. These were considered to be the key synthetic steps necessary to complete the effort.

As mentioned, the conversion of (−)-**7** to laurene (+)-**2** required stereoselective introduction of the monomethyl substituent to give **8**. However, **9** would also be useful, if enolization/protonation could be performed. A wide range of reaction conditions, solvents, and additives were surveyed, but competitive formation of the dimethylated product **10** became a serious problem. The optimum conditions were revealed by use of LDA and methyl iodide in THF/DMPU at −55 °C to provide a 38% yield of **8** and **9** as a nearly 1:1 mixture of epimers. Only a trace of gem dimethylated product **10** was observed under these conditions and 47% of the starting material **7** was recovered unchanged which, in principle, could be recycled to **8/9**. The mixture of **8** and **9** was found to be inseparable by various chromatographic efforts, but more interesting was the prospect of converting **9** to the requisite thermodynamically less-stable epimer **8**.



8 favored over **9** (8:1, Table 1, entry 8)

We envisioned that formation of the common lithium enolate of **8** and **9**, followed by a kinetic proton quench using an appropriate proton source, could result in the preferential formation of **8**. Initial attempts were performed by direct addition of the proton source to a stirred solution of the lithium enolate in THF at low temperature (Table 1, entries 1–5) and it was found that tertiary alcohols provided the best selectivity.[4] However, these experiments suffered from a lack of reproducibility,

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(1) For a review, see: Romo, D.; Meyers, A. I. *Tetrahedron* **1991**, *47*, 9503.

(2) Meyers, A. I.; Lefker, B. A. *J. Org. Chem.* **1986**, *51*, 1541. Chiral lactam **5**, listed herein as the (+)-enantiomer, was inadvertantly listed previously as the (+)-enantiomer, when it should have been (−).

(3) Nemoto, H.; Nagamochi, M.; Fukumoto, K. *J. Chem. Soc., Perkin Trans.* 1 **1993**, 2329, and references therein. For an asymmetric synthesis of (+)-epilaurene, see: Fadel, A.; Canet, J.-L.; Salaün, J. *Tetrahedron: Asymmetry* **1993**, *4* (1), 27.

(4) The selectivity was assessed by observing the chemical shifts of the newly introduced methyl group. When the 4-tolyl and 5-methyl substituents are oriented *cis*, an upfield shift of approximately 0.5 ppm for the methyl doublet is observed relative to the *trans* orientation.

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Scheme 1

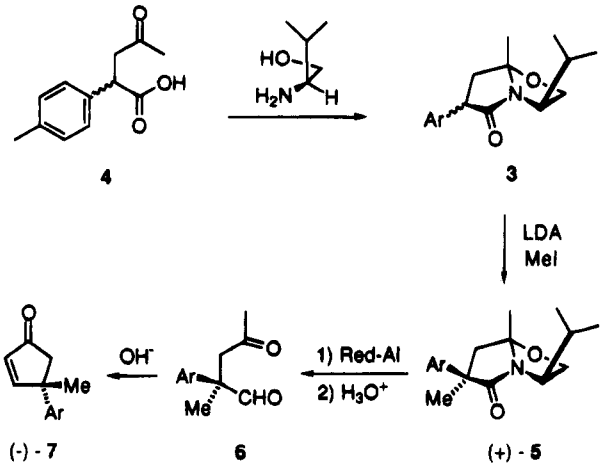
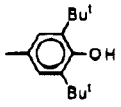
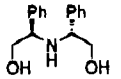


Table 1. Kinetic Protonation of Enolate of 8 and 9

entry	proton source	equiv	quench procedure[a]	quench temp (°C)	ratio **8:9**[b]	yield (%)[c]
1	methanol	1.2	A	−78	37:63	
2	*tert*-butyl alcohol	70	A	−78	85:15	83
3		15	A	−100	65:35	
4		1.2	A	−78	43:57	51
5		2.0	A	−100	80:20	67
6	ethyl salicylate	4.0	B[d]	−100	70:30	85
7	*tert*-amyl alcohol	10	B[d]	−100	87:13	71
8	*tert*-butyl alcohol	20	B[d]	−100	89:11	79−84

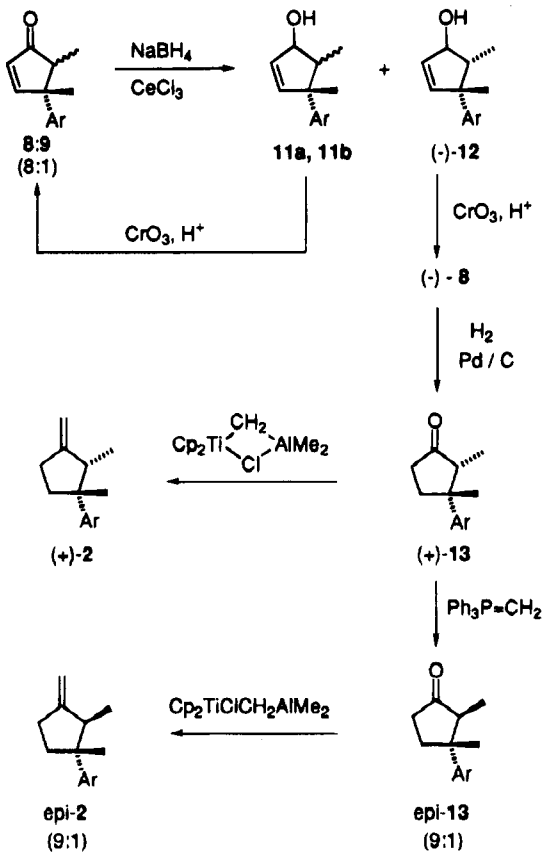
[a] Proton source added according to quenching procedure: (A) addition of a solution of the proton source in THF to a solution of the enolate via syringe; (B) dropwise addition of a solution of the enolate to a solution of the proton source in THF at constant temperature, see Experimental Section. *b* Determined by integration of the α-methyl doublets in the ^{1}H NMR spectrum. [c] Yield refers to isolated, purified material. [d] A detailed description and drawing of the transfer apparatus is shown in supporting information.

presumably due to the difficulty associated with controlling the reaction temperature under these conditions.

Krause has recently reported the use of ethyl salicylate in a similar diastereoselective protonation[5] and noted that efficient transfer of the enolate to the proton source was necessary to obtain the highest diastereoselectivity. A low-temperature transfer apparatus consisting of two round-bottomed flasks connected by a glass tube was used to effect the transfer of enolate to proton source at a constant temperature and at a controlled rate. Use of this apparatus (Table 1, ref d) provided reproducible ratios of **8:9**. The results of these experiments are summarized in Table 1, entries 6−8.

Having obtained **8** as the major component (8:1) of the mixture meant that, assuming no epimerization in the alkene reduction or methylenation steps, an 8:1 mixture

Scheme 2



of laurene and its epimer could be expected. However, it was found that pure **8** could indeed be obtained by Luche[6] reduction of the cyclopentanone mixture **8/9**, separation of the diastereomers, and oxidation of the appropriately purified allylic alcohol. The majority (59%) of the reduction products was found to be an inseparable 5:1 mixture of allylic alcohols **11a** and **11b** (Scheme 2). The remaining allylic alcohol (−)-**12** was separated (33%) and was determined to be a single diastereomer containing the 4-tolyl and the 5-methyl groups in the desired *cis* orientation (^{1}H NMR).[4] The relative configuration of the hydroxyl-bearing carbon was of no consequence and thus not determined. It was also found that **11a** and **11b** could be recycled through Jones oxidation and subsequent $NaBH_4$−$CeCl_3$ reduction to the diastereomerically pure **12** in 52% overall yield from the **8/9** mixture. Oxidation of the combined samples of **12** with Jones reagent in acetone furnished pure (−)-**8** in 99% yield which was hydrogenated to (+)-**13** in 95% yield.

Methylenation of **13**, without epimerization of the α-methyl substituent, has previously been addressed in alternate syntheses[7] of laurene, one of which used the method of Coates[8] to provide laurene from **13** in a three-step process in 24% overall yield. A recent synthesis[3] employed the method of Nozaki[9] which led to laurene in 40% yield. In the present route, the Tebbe reagent[10] for methylenation was employed providing (+)-laurene (**2**)

(5) Krause, N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1764.

(6) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226.

(7) McMurry, J. E.; von Beroldingen, L. A. *Tetrahedron* **1974**, *30*, 2027.

(8) Sowerby, R. L.; Coates, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 4758.

(9) (a) Takai, K.; Hatta, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, 2417. (b) Hibino, J.; Okazoe, T.; Takai, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5579, 5581. (c) Lombardo, L. *Org. Synth.* **1987**, *65*, 81.

(10) Pine, S. H.; Kim, G.; Lee, V. *Org. Synth.* **1990**, *69*, 72.

in 56% yield after Kugelrohr distillation. Comparison of the sign of rotation of (+)-**2** ($[\alpha]^{23}_D$ + 37.8) derived from (−)-**7** with that of natural laurene[11] ($[\alpha]^{23}_D$ + 48.7) indicated that the correct absolute configuration was obtained via this route. Nevertheless, comparison of the magnitude of the rotation reported for natural laurene with that obtained herein indicated an optical purity of only 78%. Furthermore, the previous synthesis[3] would only be 71% ee on the basis of this data. To assess the origin of the polarimetric discrepancy, dimethylcyclopentenone **10**, also derived from (−)-**7**, was reduced to afford (+)-α-cuparenone **1** in 89% yield. The optical rotation of the latter ($[\alpha]^{23}_D$ +163) indicated it possessed an optical purity of at least 96% (lit.[12] $[\alpha]_D$ +170). Additional proof of purity was gathered by subjecting a 3:1 mixture of methyl cyclopentanones **13** and *epi*-**13** to phosphonium ylide conditions such that both epimers were accessed. This would indicate whether (+)-**2** was contaminated by *epi*-**2**. Surprisingly, addition of methylenetriphenylphosphorane did not give, as expected,[13] the olefin *epi*-**2**, but only returned a 9:1 mixture of unreacted *epi*-**13** and **13** in 58% yield. Subsequent methylenation of the mixture (**13**) with the Tebbe reagent did furnish a 9:1 mixture of *epi*-**2** and **2**. Comparison of the ^{1}H NMR spectra of (+)-**2** and the latter mixture confirmed that no *epi*-**2** was present in the final sample of (+)-**2**. Thus, the discrepancy in the magnitude of the specific rotation between the reported natural and synthetic product was not due to impurity by *epi*-**2**. One is then left to conclude that the discrepancy in specific rotation was due solely to polarimetric factors regarding the isolation,[11] since no racemization is possible at the quaternary carbon of the intermediates **5**−**13**. Due to above corrections carried out to assess the rotation, it is also quite possible that the optical purity of the Fukumoto product[3] is higher than that reported (i.e. 92% based on $[\alpha]_D$ + 37.8).

In summary, the total synthesis of (+)-laurene (**2**) has been completed in 10% yield from (−)-**7** utilizing chiral, nonracemic bicyclic lactams. Diastereoselective kinetic protonation of a chiral lithium enolate with a sterically demanding proton source provided the unfavored thermodynamic diastereomer found in the natural product. Furthermore, methylenation, without epimerization, proceeded smoothly using the Tebbe reagent. Enantiomeric purity was assessed via the synthesis of (+)-cuparenone (**1**) from (−)-**7**, and found to be no less than 96%. The possibility of contamination of (+)-**2** by *epi*-**2** was ruled out by the synthesis of a mixture of the two compounds and comparison of their NMR spectra. Finally, the specific rotation for natural (+)-laurene as reported previously has been found to be too high and was corrected as above.

Experimental Section

Thin layer chromatography (TLC) and flash chromatography were performed with E. Merck or Amicon Matrix silica gel (230−400 mesh). All reagents were purchased from Aldrich. Unless otherwise stated, all reactions were conducted under an argon atmosphere in flame-dried apparatus. Tetrahydrofuran was distilled from sodium−benzophenone ketyl under argon atmosphere prior to use. DMPU was distilled from calcium hydride under reduced pressure prior to use.

(*R*)-4,5-Dimethyl-4-*p*-tolylcyclopentenones 8 and 9. Alkylation of 7. To a stirred solution of diisopropylamine (363 μL, 2.59 mmol) in 3.0 mL of THF at 0 °C was added *n*-butyllithium (2.00 M solution in hexanes, 1.26 mL, 2.52 mmol) followed by DMPU (1.8 mL). The solution was stirred for 15 min and then cyclopentenone **7**[14] (276 mg, 1.48 mmol) in 2.5 mL of THF was added dropwise. The solution was stirred for 30 min at 0 °C and then cooled to −70 °C. Methyl iodide (147 μL, 2.37 mmol) was added in one portion and stirring continued for 3 h at −70 °C. The temperature was raised to −55 °C, stirred for 13 h, raised to 0 °C and stirred for 30 min, and finally raised to ambient temperature and stirred for 10 min. The reaction was quenched with saturated NH_4Cl (aq) (2 mL), and the layers were separated. The aqueous layer was diluted with water (5 mL) and extracted with ether (10 mL), and the combined organics were washed with brine (15 mL), dried ($MgSO_4$), and concentrated. Flash chromatography of the residue (8:1, hexanes:ethyl acetate) provided 112 mg (38%) of a 53:47 ratio of **8** and **9** as a colorless oil.

(*R*)-4,5-Dimethyl-4-*p*-tolylcyclopentenones 8 and 9. Proton Quench of Enolates (Method B). To a stirred solution of diisopropylamine (87 μL, 0.62 mmol) in 3.0 mL THF at 0 °C was added *n*-butyllithium (2.00 M solution in hexanes, 293 μL, 0.60 mmol). The solution was stirred for 15 min and then a mixture of methylcyclopentenones **8** and **9** (80 mg, 0.40 mmol) in 2.0 mL of THF was added dropwise. The solution was stirred at 0 °C for 30 min and then transferred via cannula to the low temperature transfer apparatus. The apparatus was cooled to −100 °C, and a solution of the enolate was transferred dropwise to a solution of *tert*-butyl alcohol (0.75 mL, 8.0 mmol) in 4.0 mL of THF over 15 min. The mixture was allowed to warm to −78 °C over a period of 15 min, and then the reaction was quenched with saturated NH_4Cl (aq) (2 mL). Sufficient water was added to dissolve the solids, and the layers were separated. The aqueous layer was extracted with ether (15 mL), and the combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), and concentrated. Flash chromatography of the residue (8:1, hexanes:ethyl acetate) provided 67 mg (84%) of an 88:12 epimeric ratio of cyclopentenones **8** and **9**.

(*R*)-4,5-Dimethyl-4-*p*-tolylcyclopentenols 11a, 11b, and 12. To a solution of cyclopentenones **8** and **9** (8:1, 157 mg, 0.78 mmol) in 4.0 of mL methanol at 0 °C was added cerium trichloride heptahydrate (365 mg, 0.98 mmol) . The mixture was stirred for 5 min, and sodium borohydride (35 mg, 0.93 mmol) was added with vigorous hydrogen evolution. The mixture was stirred for 10 min, diluted with ether (5 mL), and poured into brine (20 mL). The organic layer was separated, dried ($MgSO_4$), and concentrated. Flash chromatography of the residue (4:1, hexanes:ethyl acetate) provided 52 mg (33%) of allylic alcohol **12** as a colorless oil and 93 mg (59%) of a mixture of allylic alcohols **11a** and **11b** as a colorless oil. **Minor product 12**: $[\alpha]^{23}_D$ −48.9 (*c* 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.61 (d, *J* = 7.4 Hz, 3H), 1.45 (s, 3H), 2.11 (m, 1H), 2.30 (s, 3H), 4.60 (dd, *J* = 2.5 Hz, *J* = 6.4 Hz, 1H), 5.98 (d, *J* = 5.7 Hz, 1H), 6.10 (dd, *J* = 2.5 Hz, *J* = 5.7 Hz, 1H), 7.13 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 10.62, 20.78, 26.39, 48.96, 53.46, 79.01, 127.16, 128.70, 131.65, 135.57, 142.17, 143.93; IR (neat) 3327, 3053, 2958, 2930, 2873, 1505, 1453, 1377, 1344, 1056, 1041, 1018, 862 cm^{-1}.

(*R*)-4,5-Dimethyl-4-*p*-tolylcyclopentenone 8. To a stirred solution of allylic alcohol **12** (99 mg, 0.49 mmol) in 5.0 mL of acetone at 0 °C was added Jones reagent (2.7 M aqueous solution, 0.61 mL, 1.65 mmol) dropwise. The solution was stirred for 10 min, and the reaction was quenched with methanol (3 mL). The mixture was diluted with water (10 mL) and extracted with ether (2 × 20 mL). The combined organic layers were washed with water (15 mL) and brine (15

(11) (a) Irie, T.; Yasunari, Y.; Suzuki, T.; Imai, N.; Kurosawa, E.; Masamune, T. *Tetrahedron Lett.* **1965**, 3619. (b) Irie, T.; Suzuki, T.; Yasunari, Y.; Kurosawa, E.; Masamune, T. *Tetrahedron*, **1969**, *25*, 459.

(12) Chetty, G. L.; Dev, S. *Tetrahedron Lett.* **1964**, 73.

(13) It had been reported (ref 11b) that when (+)-**13** was treated with sodium hydride and methyltriphenylphosphonium bromide in DMSO *epi*-(−)-**2** was obtained in ca. 80% yield.

(14) (−)-**7** was prepared from *p*-tolylacetic acid according to the procedures previously described (see ref 2 above), and the physical and spectral properties of **3**−**7** were identical with those reported previously for the (*S*)-enantiomers.

mL), dried twice ($MgSO_4$), and concentrated to yield 97 mg (99%) of cyclopentenone **8** as a colorless oil. $[\alpha]^{23}_D$ −75.1 (*c* 0.55, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 0.61 (d, *J* = 7.5 Hz, 3H), 1.63 (s, 3H), 2.28 (q, *J* = 7.4 Hz, 1H), 2.30 (s, 3H), 6.27 (d, *J* = 5.7 Hz, 1H), 7.10 (m, 4H), 7.52 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.27, 20.81, 25.70, 51.60, 53.27, 127.02, 128.94, 131.09, 136.40, 138.30, 169.38, 212.30; IR (neat) 2969, 2924, 2870, 1710, 1508, 1450, 1160 cm^{-1}; HRMS (FAB, M + H) calcd for $C_{14}H_{16}O$ 200.1202, found 200.1196.

(*R*)-4,5-Dimethyl-4-*p*-tolylcyclopentanone 13. To a solution of cyclopentenone **8** (97 mg, 0.49 mmol) in 4.0 mL of ethyl acetate was added 10% palladium on carbon (15 mg). The reaction vessel was evacuated and purged three times with hydrogen and then stirred under 1 atm of hydrogen for 1 h. The mixture was gravity filtered and concentrated to yield 93 mg (95%) of cyclopentanone **13** as a colorless oil: $[\alpha]^{25}_D$ +49.0 (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.81 (d, *J* = 7.3 Hz, 3H), 1.39 (s, 3H), 2.05 (m, 1H), 2.31 (s, 3H), 2.42 (m, 3H), 7.08 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 11.79, 20.80, 29.73, 32.17, 35.00, 46.29, 55.22, 126.46, 129.00, 135.55, 142.24, 221.13; IR (neat) 2956, 2923, 1741, 1655, 1560, 1515, 1458, 1155 cm^{-1}; HRMS (FAB, M + H) calcd for $C_{14}H_{18}O$ 203.1437, found 203.1432. Spectral properties were identical with those reported previously.[3]

(*R*)-4,5-Dimethyl-4-*p*-tolylcyclopentanones *epi*-13 and 13. To a slurry of methyltriphenylphosphonium bromide (1.63 g, 4.57 mmol) in 50 mL of THF at −78 °C was added *n*-butyllithium (2.00 M solution in hexanes, 2.16 mL, 4.35 mmol). The mixture was stirred at −78 °C for 15 min, warmed to 0 °C and stirred for 15 min, and then cooled to −78 °C at which time a mixture of cyclopentanones **13** and *epi*-**13** (3:1, 88 mg, 0.44 mmol) in 2.5 mL of THF was added dropwise. The mixture was stirred at −78 °C for 15 min, warmed to 0 °C and stirred for 15 min, and then warmed to ambient temperature, stirred for 2 h, quenched with water (5 mL), and concentrated. The residue was dissolved in water (50 mL) and extracted with hexanes (2 × 40 mL). The combined organic layers were washed with water (30 mL), brine (30 mL), dried (Na_2SO_4), and concentrated. The nonpolar compounds were removed by elution with hexanes through standard alumina, and elution with ethyl acetate provided a 9:1 ratio of *epi*-**13** and **13** as a colorless oil (58%).

(+)-Laurene (2). To a stirred solution of the Tebbe reagent[15] (1.84 mL, 1.84 mmol) at 0 °C was added dropwise methylcyclopentanone **13** (93 mg, 0.46 mmol) in 1.84 mL of THF. The solution was allowed to warm to ambient temperature after addition and stirred for 1 h. The mixture was diluted with ether (1 mL); then the reaction was quenched by cautious addition of 20 drops of 10% NaOH (aq), resulting in vigorous evolution of methane. Sodium sulfate (0.5 g) was added, and the mixture was filtered through a 3 cm pad of Celite. Chromatography of the residue obtained by concentration on neutral alumina (neat hexanes) provided crude (+)-laurene (**2**) as a pale yellow oil. The oil was Kugelrohr distilled (100 °C, 0.1 mmHg) to provide 50 mg (56%) of (+)-laurene (**2**) as a colorless oil: $[\alpha]^{23}_D$ +37.8 (*c* 1.16, EtOH); ^1H NMR ($CDCl_3$) δ 0.70 (d, *J* = 7.1 Hz, 3H), 1.27 (s, 3H), 1.79 (m, 1H), 2.23 (m, 1H), 2.31 (s, 3H), 2.54 (m, 3H), 4.86 (m, 2H), 7.10 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 17.16, 20.84, 29.11, 29.59, 34.55, 48.88, 50.40, 105.49, 126.81, 128.54, 134.72, 144.38, 157.45; IR (neat): 3060, 2959, 2922, 2867, 1656, 1514, 1454, 1371, 1017, 879, 814 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{20}$ 200.1566, found 200.1559. Spectral properties were identical with those reported previously.[3]

(*R*)-(+)-α-Cuparenone (1). To a stirred solution of dimethylated cyclopentenone **10** (32 mg, 0.15 mmol) in 2.0 mL of ethyl acetate was added 10% palladium on carbon (9 mg). The reaction vessel was evacuated and purged three times with hydrogen and then stirred under 1 atm of hydrogen for 1 h. The mixture was gravity filtered and concentrated. Flash chromatography of the residue (8:1, hexanes:ethyl acetate) provided 29 mg (89%) of (+)-α-cuparenone (**1**) as a crystalline solid, mp 53−54 °C: $[\alpha]^{23}_D$ +163 (*c* 0.82, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.60 (s, 3H), 1.16 (s, 3H), 1.24 (s, 3H), 1.90 (m, 1H), 2.33 (s, 3H), 2.40 (m, 2H), 2.60 (m, 1H), 7.21 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 18.36, 20.78, 22.07, 25.29, 29.61, 33.72, 48.26, 53.15, 126.33, 128.85, 135.75, 141.86, 222.51; IR (neat) 2964, 2928, 2874, 1737, 1514, 1460, 1375, 1273, 1094, 1054, 818 cm^{-1}; HRMS (FAB, M + H) calcd for $C_{15}H_{20}O$ 217.1593, found 217.1578. Spectral properties were identical with those reported previously for the (−) enantiomer.[2]

Acknowledgment. Financial support for this work was kindly provided by the National Institutes of Health. We are grateful to Professor G. Helmchen (Heidelberg) for a description of the low-temperature transfer apparatus (see supporting information for diagram).

Supporting Information Available: ^1H and ^{13}C NMR spectra of **1**, **2**, **7**, **8**, **12**, and **13** and a 9:1 mixture of *epi*-**2** and **2** (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(15) The Tebbe reagent was prepared as a 1.0 M solution in toluene according to the procedure previously described (see ref 10 above).