Anal. Calcd for $C_{26}H_{15}N_3O_7$: C, 64.86; H, 3 14; N, 8.73. Found: C, 65.32; H, 3.45; N, 8.57.

2',4-Bis(4-hydroxybutyl)cyclohexylbenzene (47). The preparation of **47** was carried out by the same method described for the preparation of **27**, utilizing the diester **31** (3.6 g, 10 mmol), $LiAlH_4$ (0.4 g, 10 mmol), and dry ether (30 mL). The product was distilled to give **47** (2.7 g, 90%): bp 204–206 °C (0.1 mm); n^{21}_D 1.5118; IR (film) 3450 cm^{-1} (OH).

2',4-Bis(4-bromobutyl)cyclohexylbenzene (48). The preparation of **48** was carried out by the same method described for the preparation of **16**, utilizing **47** (2.5 g, 8.2 mmol), 47% HBr solution (5.2 g, 31 mmol), and concentrated H_2SO_4 (1 g). Distillation of the product gave the bromide **48** (2.7 g, 75%(: bp 193–195 °C (0.1 mm); n^{16}_D 1.5499.

2',4-Di-*n*-butylcyclohexylbenzene (49). A solution of **48** (1.0 g, 2.3 mmol) in dry tetrahydrofuran (5 mL) was added dropwise to a suspension of $LiAlH_4$ (0.4 g, 10 mmol) in dry tetrahydrofuran (8 mL) during 15 min. The reaction mixture was refluxed with stirring for 10 h, and the excess reducing agent was decomposed with ethyl acetate. After the mixture was acidified with diluted HCl solution, the organic phase was extracted with ether. After workup in the usual manner, the product was distilled to give **49** (0.5 g, 80%): bp 148–150 °C (1.0 mm); n^{20}_D 1.5121.

Anal. Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84. Found: C, 88.24; H, 11.79.

2,4'-Di-*n*-butylbiphenyl (50). The hydrocarbon **49** (0.4 g, 1.47 mmol) was dehydrogenated by heating at 250–280 °C for 1 h with 10% palladium on carbon (40 mg). Distillation of the oily product gave **50** (3.5 g, 90%): bp 112–114 °C (0.5 mm); n^{19}_D 1.5198.

Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.20; H, 9.81.

Registry No.—**5a,** 69597-38-2; **5b,** 792-28-9; **5c,** 69597-39-3; **5d,** 899-75-2; **9,** 69597-22-4; **14a,** 69597-20-2; **14b,** 69651-44-1; **14c,** 69597-21-3; **14d,** 69651-19-0; **15,** 69597-23-5; **16,** 69597-24-6; **17,** 69597-25-7; **18,** 69597-05-3; **19,** 4099-77-8; **20,** 69597-01-9; **21,** 69597-08-6; **22,** 69597-12-2; **23,** 69597-16-6; **24,** 69597-26-8; **25,** 69597-06-4; **26,** 69597-27-9; **27,** 69597-28-0; **27** phenylurethane, 69597-29-1; **28,** 69597-30-4; **29,** 69597-02-0; **30,** 69597-09-7; **31,** 69597-13-3; **32,** 69597-17-7; **34,** 50-32-8; **34** picrate, 5929-01-1; **35,** 69597-07-5; **36,** 69597-31-5; **37,** 69597-03-1; **38,** 69597-10-0; **39,** 69597-14-4; **40,** 69597-18-8; **42,** 69597-04-2; **43,** 69597-11-1; **44,** 69597-15-5; **45,** 69597-19-9; **47,** 69597-32-6; **48,** 69597-33-7; **49,** 69597-34-8; **50,** 69597-35-9; diethyl [2(2-phenylcyclohexyl)ethyl]-propanedioate, 69597-36-0; [2-(2-phenylcyclohexyl)ethyl]propenedioic acid, 69597-37-1; sodium ethylmalonate, 996-82-7.

Supplementary Material Available: Figure 1, showing the NMR spectra of 2'-4-polymethylenecyclohexylbenzenes, Figure 2, showing the NMR spectra of 2,4'-polymethylenebiphenyls, Figure 3, showing the UV spectra of 2',4-polymethylenecyclohexylbenzenes, and Figure 4, showing the UV spectra of 2,4'-polymethylenebiphenyls (4 pages). Ordering information is given on any current masthead page.

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Determination of Enantiomeric Purity of Chiral Lactones. A General Method Using Nuclear Magnetic Resonance[1]

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A general method is described for determining enantiomeric purities of chiral lactones, regardless of their ring size. The approach involves treatment of a lactone with methyllithium, followed by NMR examination of the diol produced in the presence of a chiral shift reagent such as $Eu(tfc)_3$. The method is broadly applicable to a wide range of variously substituted γ-, δ-, and ϵ-lactones. Its accuracy for enantiomeric excess determinations is ±3%. This has been confirmed using selected optically active lactones of established optical purities.

The development of asymmetric syntheses of chiral lactones, for use as synthons and as target molecules, is receiving increasing attention from both the chemical[2,3] and enzymic[4] directions. As a result, a pressing need has arisen for accurate and convenient methods for evaluating their enantiomeric purities. Optical rotation criteria have been used almost exclusively until very recently, despite the fact that the unreliability of optical methods is well documented.[5] However, although direct enantiomeric excess (ee) determination techniques are recognized as being much preferred, neither of the two lactone ee determination methods[6,7] reported so far is generally applicable. The GLC approach,[6] involving conversion of the lactone to an orthoester with (2*R*,3*R*)-2,3-butanediol, works well with δ-lactones. However, all attempts to extend it to γ-lactone analyses have been unsatisfactory.[8] The NMR method,[7] which utilizes chiral solvating agents, has been applied to both γ- and δ-lactones. For geometric reasons, it is most effective for γ-lactone structures.

Direct methods for ee determination are becoming increasingly dominated by chiral NMR shift reagent techniques.[10] These methods have proven spectacularly successful with chiral molecules possessing a broad range of functional groups. Disappointingly, although chiral shift reagent analyses of esters are well documented,[3b,10b,11] optical purities of lactones cannot be measured using the chiral shift reagents currently available.[1,3b] This problem has now been overcome by reacting the lactones (**1**) with methyllithium (Scheme I) followed by NMR examination of the resulting diols (**2**) in the

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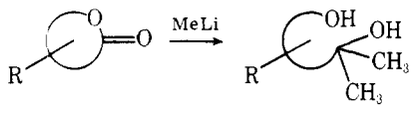
Scheme I

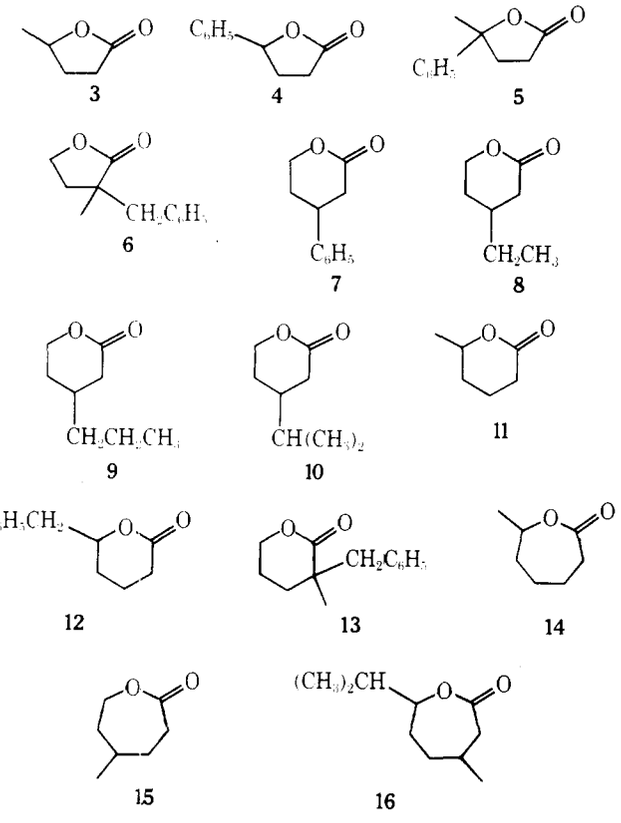


1 2

presence of a chiral lanthanide shift reagent. This method is a generally applicable one. It is not restricted by the size of the lactone ring.

Results

The structural range of chiral γ-, δ-, and ε-lactones surveyed is represented by formulas **3–16.** These compounds were purchased (**3**), were available from previous studies (**7–10**),



3 4 5 6 7 8 9 10 11 12 13 14 15 16

or were prepared by literature methods or by unexceptional alternative routes.

Each compound was reacted with 3 equiv of methyllithium in tetrahydrofuran as indicated in Scheme I, and the corresponding diols **17–30** were isolated and characterized. For ee determinations, the reactions were repeated on a 5-mg scale. The diol products were then subjected directly, without purification, to NMR examination in carbon tetrachloride in the presence of varying proportions of tris[(trifluoromethyl)-hydroxymethylene-*d*-camphorato]europium(III) [Eu(tfc)$_3$; Optishift I]. The chemical shift differences ($\Delta\Delta\delta$) observed for the various enantiotopic and diastereotopic groups of the diols **17–30** are recorded in Table I. At the shift reagent concentrations indicated, the peak separations are sufficient to permit accurate integration of all of the designated resonances. As expected, the relative peak areas were 1:1 for the racemic diols surveyed. The viability of the method for determining ee's of optically active lactones was confirmed in two independent ways. The 3-ethyl lactone **8**, 65% enantiomerically pure by the orthoester GLC analysis,[4c,6] and optically active samples of the (−)-methone derived diol **30** (made up as 25 and 75% optically pure, by weight) were measured as 67, 28, and 74% ee, respectively, by the current NMR method using the Eu(tfc)$_3$ concentrations shown in Table I. The routine accuracy of the technique is considered to be ±3%.

Discussion

The lack of success encountered in attempting to determine ee levels of chiral lactones using chiral shift reagents is directly attributable to the weak coordinating capabilities of both the carbonyl and the ether moities of the lactone function. Conversion of lactones to alcohol derivatives thus presented itself as an attractive solution to the problem since the ability of hydroxyl groups to coordinate strongly with lanthanide shift reagents is well documented.[10]

Methyllithium was chosen as the reagent for several reasons. Its reaction with lactones to give diols of general structure **2** is rapid, quantitative, and introduces the *gem*-dimethyl function, a group which is easily visible and instantly identifiable in the NMR spectrum. Furthermore, diols **2** possess both primary and tertiary alcohol functions. This structural feature is important since it allows for the possibility of lanthanide complexation at either hydroxyl group, or at both simultaneously by appropriate expansion of the coordination shell.[12] Although on steric grounds the primary hydroxyl should be the more readily complexed of the two, the contribution of coordination at the tertiary alcohol group must not be ignored.[13] Differential or concurrent coordination of the shift reagent with the two hydroxyl sites was expected to magnify the various NMR-observable diastereomeric differences in the complexes.

The reaction with methyllithium is a very straightforward procedure, and only 3–5 mg of lactone is required for an accurate ee determination. The diol product obtained by simple workup is of >95% purity and requires no additional purification. It is simply dissolved in carbon tetrachloride[14] and analyzed in the presence of up to ~0.4 equiv of Eu(tfc)$_3$. Increasing the shift reagent concentration beyond this level soon becomes counterproductive, with the $\Delta\Delta\delta$ values either remaining constant or decreasing.[10,12] The optimum proportion of Eu(tfc)$_3$ varies, but for many diols it is in the neighborhood of ~0.25 equiv. Before the final spectrum is recorded, it is advisable to filter the solution (through a small cotton plug) in order to remove any europium oxide particles present since these tend to broaden the peaks.[10b] Also, for those diols, such as **17, 19, 20, 25,** and **27–29,** with spectra containing overlapping and difficult to identify resonances, the addition of a small amount of (<0.125 equiv) of Eu(tfc)$_3$ assures the correct assignment of all of the important proton peaks.

Eu(tfc)$_3$ gave satisfactory results with each of the diols listed in Table I. However, the technique can clearly be extended to the full range of chiral shift reagents available[10] in any situation where inadequate enantiomeric shift differences are encountered. All of the Table I data were recorded with a 100-MHz spectrometer. For enantiomeric shift differences of >0.06 ppm, we have also found 60-MHz spectra to be quite satisfactory. For $\Delta\Delta\delta$ values of <0.03 ppm, measurements at 220 MHz are desirable. The operational accuracy of the method is ±3%. This was determined from the 1:1 peak ratios observed for the racemic diols **17–30** and confirmed by comparison of the NMR-derived ee's of optically active samples of diols **22** and **30.** These were obtained from lactones **8** and **16,** respectively, of established optical purities.

As Table I shows, the resonances of most general value for ee determinations are those of the diastereotopic methyl groups of the $(CH_3)_2C(OH)$ functions. However, each diol contains several other spectroscopically nonequivalent functions whose different proton resonances can also be used. Some of these are indicated in Table I. In addition, some ortho protons of the phenyl-containing diols exhibited promising splitting patterns. While singlet peaks, as in the spectra of **19** and **20,** are clearly the easiest to monitor, ee determinations based on doublet (**17, 24**) or triplet (**22, 23**) resonances present no difficulty with the more than adequate $\Delta\Delta\delta$ values of Table I.

Table I. Enantiomeric Shift Differences Observed[a]

lactone	diol product	no.	resonance obsd $\Delta\Delta\delta$, ppm	equiv of $Eu(tfc)_3$
(±)-3	$\mathbf{CH_3}CH(OH)(CH_2)_2C(OH)(CH_3)_2$	(±)-17	0.08 (**H**)	0.30
(±)-4	$C_6H_5CH(OH)(CH_2)_2C(OH)(\mathbf{CH_3})_2$	(±)-18	0.16(**H**)	0.27
(±)-5	$C_6H_5C(OH)(\mathbf{CH_3})(CH_2)_2C(OH)(CH_3)_2$	(±)-19	0.79(**H**)	0.23
			0.10(*H*)	0.23
(±)-6	$HO(CH_2)_2C(CH_2C_6H_5)(CH_3)C(OH)(\mathbf{CH_3})_2$	(±)-20	0.13(**H**)	0.25
			0.06(*H*)	0.25
(±)-7	$HO(CH_2)_2CH(C_6H_5)CH_2C(OH)(\mathbf{CH_3})_2$	(±)-21	0.04(**H**)	0.25
(±)-8	$HO(CH_2)_2CH(CH_2\mathbf{CH_3})CH_2C(OH)(CH_3)_2$	(±)-22	0.04(**H**)	0.26
(±)-9	$HO(CH_2)_2CH(CH_2CH_2\mathbf{CH_3})CH_2C(OH)(CH_3)_2$	(±)-23	0.025(**H**)	0.42
(±)-10	$HO(CH_2)_2CH[CH(\mathbf{CH_3})_2]CH_2C(OH)(CH_3)_2$	(±)-24	0.06(**H**)	0.40
(±)-11	$CH_3CH(OH)(CH_2)_3C(OH)(\mathbf{CH_3})_2$	(±)-25	0.08(**H**)	0.25
(±)-12	$C_6H_5CH_2CH(OH)(CH_2)_3C(OH)(\mathbf{CH_3})_2$	(±)-26	0.20(**H**)	0.32
(±)-13	$HO(CH_2)_2C(\mathbf{CH_2}C_6H_5)(CH_3)C(OH)(CH_3)_2$	(±)-27	0.14(**H**)	0.12
(±)-14	$\mathbf{CH_3}CH(OH)(CH_2)_4C(OH)(CH_3)_2$	(±)-28	0.06(**H**)	0.25
(±)-15	$HO(CH_2)_2CH(CH_3)(CH_2)_2C(OH)(\mathbf{CH_3})_2$	(±)-29	0.025(**H**)	0.20
(±)-16	$(\mathbf{CH_3})_2CHCH(OH)(CH_2)_2CH(CH_3)CH_2C(OH)(CH_3)_2$	(±)-30	0.44(**H**)	0.25
			0.02(*H*)	0.25

[a] Spectra were determined at 100 MHz on CCl_4 solutions. When $\Delta\Delta\delta < \sim 0.03$ ppm, measurement at 220 MHz is recommended.

The technique is not recommended as the basis of an absolute configuration correlation method. It suffers from the same uncertainties noted previously in that the directions in which enantiomeric groups shift in the presence of shift reagent are unpredictable.[10b,11b] For example, the relative positions of the structurally analogous monomethyl and dimethyl resonances of **17** and **25** are unexpectedly reversed in the presence of $Eu(tfc)_3$.

Unsymmetrical diols of type **2** will always contain several different enantiotopic or diastereotopic groups which can be monitored. This is a particularly valuable feature of the method since it virtually ensures that at least one key resonance will be clearly visible when those of others overlap or are masked, or have $\Delta\Delta\delta$ values that are too small.

From the broad and representative structural range of the lactones **3–16** surveyed, it is clear that this ee determination method is generally applicable to chiral lactones, regardless of their ring size. We consider that the key to its versatility and flexibility lies in the fact that interactions of the diols **2** with the shift reagent give rise to particularly rigid complexes. The complexes are especially geometrically constrained by the steric requirements of the *gem*-dimethyl function. Bidentate coordination of both hydroxyl groups with the lanthanide may also be a rigidifying factor. The inflexible complexes which result therefore provide the various enantiotopic or diastereotopic groups present with the well-defined different chiral environments needed to give the cleanly separated NMR peaks required for facile ee determinations. The method is now in routine use in our laboratories.

Experimental Section[15]

Preparation of Lactones 3–16. 4-Hydroxypentanoic acid lactone (**3**) was purchased from Aldrich. Lactones **7–10** were available from previous studies,[4] and **4**,[16] **5**,[17] **11**,[18] **14**,[19] and **15**[19] were prepared by literature methods, or straightforward variations thereof.

2-Benzyl-4-hydroxy-2-methylbutanoic Acid Lactone (6). The general method of Herrmann and Schlessinger[20] was used. γ-Butyrolactone (15 g, 0.174 mol) in tetrahydrofuran (175 mL) was added via syringe with stirring at −78 °C to lithium diisopropylamide (0.174 mol) in tetrahydrofuran (70 mL). After 20 min, benzyl chloride (24.2 g, 0.191 mol) in hexamethylphosphoramide (35 mL) was added dropwise with stirring. The temperature was then raised to −40 °C for 1 h. The mixture was then acidified with 10% aqueous hydrochloric acid and extracted with ether. The ether extract was washed with saturated aqueous sodium bicarbonate, dried (K_2CO_3), and evaporated. The crude product obtained was immediately alkylated again with methyl iodide using an identical procedure. The final product was Kugelrohr distilled (120 °C, 1 mm) to give lactone **6** (33 g, 40%): ^1H NMR δ 1.24 (3 H, s), 1.58–2.54 (2 H, m), 2.86 (2 H, d of d, J = 13 Hz), 3.46–4.3 (2 H, m), and 7.20 (3 H, s).

5-Benzyl-5-hydroxypentanoic Acid Lactone (12). 2-Benzylcyclopentanone, prepared from cyclopentanone using Stork's enamine method,[21] was treated with *m*-chloroperbenzoic acid according to the general method of Starchen and Phillips.[19] The lactone **12** was obtained in 85% yield after Kugelrohr distillation (120 °C, 1 mm): ^1H NMR δ 1.10–2.20 (4 H, m), 2.30–2.72 (2 H, m), 2.72–3.32 (2 H, m), 4.50 (1 H, m), and 7.22 (5 H, s).

2-Benzyl-5-hydroxy-2-methylpentanoic Acid Lactone (13). Allylbenzylacetic acid[22] was converted to 2-benzylpentanoic acid lactone by the general method of Westman[23] and then methylated as described above for lactone **6**. The product was Kugelrohr distilled (120 °C, 1 mm) to give lactone **13** (60% yield): ^1H NMR δ 1.30 (3 H, s), 1.50–2.12 (4 H, m), 3.00 (2 H, d of d, J = 13 Hz), 4.22 (2 H, m), and 7.24 (5 H, s).

6-Hydroxy-6-isopropyl-3-methylhexanoic Acid Lactone (16). Both the racemic and (−)-lactones were prepared in 80% yields from (±)- or (−)-menthone[24] by Baeyer–Villiger oxidation[25] with *m*-chloroperbenzoic acid. Both lactones (−)- and (±)-**16** had bp 82 °C (3 mm); mp 45–46 °C (lit.[25] (±) mp 46–48 °C); ^1H NMR δ 1.00 (6 H, d, J = 7 Hz), 1.10 (3 H, d, J = 6 Hz), 1.10–2.30 (6 H, m), and 4.10 (1 H, m). The (−) enantiomer had $[\alpha]^{25}_D$ −22.0° (*c* 2, $CHCl_3$).

Conversion of Lactones 3–16 to Diols 17–30. The same general procedure was followed in each case. Methyllithium (3 equiv) was added with stirring to 1 equiv of the lactone in tetrahydrofuran at −78 °C. The mixture was then allowed to warm to 20 °C and stirred at this temperature for a further 1 h. The mixture was then neutralized with 10% aqueous acetic acid and extracted with ether. The ether solution was washed with aqueous sodium bicarbonate, dried (K_2CO_3), and evaporated, and the product was distilled or recrystallized. The properties of the diols prepared in this manner were the following.

2-Methyl-2,5-hexanediol (17 from 3): 80% yield; bp 116–118 °C (5 mm) [lit.[26] bp 107 °C (4 mm)]; ^1H NMR δ 1.18 (3 H, d, J = 6 Hz), 1.20 (6 H, s), 1.38–1.80 (4 H, m), 3.70 (1 H, m), and 3.82 (2 H, broad s).

4-Methyl-1-phenyl-1,4-pentanediol (18 from 4): 80% yield; mp 74–75 °C; ^1H NMR δ 1.14 (6 H, s), 1.36–2.00 (6 H, m), 4.58 (1 H, m), and 7.26 (5 H, s). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.33. Found: C, 74.37; H, 9.43.

2-Methyl-5-phenyl-2,5-hexanediol[27] (19 from 5): 71% yield after Kugelrohr distillation (120 °C, 1 mm); ^1H NMR δ 1.18 (3 H, s), 1.56 (3 H, s), 1.10–1.20 (4 H, m), 3.06 (2 H, s), and 7.36 (5 H, m).

3-Benzyl-3,4-dimethyl-1,4-pentanediol (20 from 6): 82% yield after Kugelrohr distillation (120 °C, 1 mm); ^1H NMR δ 0.82 (3 H, s), 1.28 (6 H, s), 1.00–1.80 (2 H, m), 2.62 (2 H, d, J = 6 Hz), 3.60 (2 H, m), and 3.88 (2 H, s). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.72; H, 9.99.

5-Methyl-3-phenyl-1,5-hexanediol (21 from 7): 85% yield after column chromatography on silica (4:1 benzene–ether elution); ^1H NMR δ 1.08 (6 H, d, J = 2 Hz), 1.50–2.00 (4 H, m), 2.62 (2 H, s), 2.70–3.20 (1 H, m), 3.42 (2 H, t, J = 5.6 Hz), and 7.28 (5 H, s). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.82; H, 9.80.

3-Ethyl-5-methyl-1,5-hexanediol (22 from 8): 66% yield; bp 122–124 °C (0.6 mm); ^1H NMR δ 0.70–1.90 (10 H, m), 1.28 (6 H, s),

2.76 (2 H, s), and 3.70 (2 H, t, J = 6 Hz). Anal. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.58. Found: C, 67.56; H, 12.48.

5-Methyl-3-propyl-1,5-hexanediol (23 from 9): 87% yield; bp 120 °C (1.5 mm); ^{1}H NMR δ 0.76–2.00 (12 H, m), 1.30 (6 H, s), 3.00 (2 H, s), and 3.78 (2 H, t, J = 6 Hz). Anal. Calcd for $C_{10}H_{22}O_2$: C, 68.92; H, 12.72. Found: C, 68.73; H, 12.75.

3-Isopropyl-5-methyl-1,5-hexanediol (24 from 10): 80% yield; bp 122–124 °C (1.9 mm); ^{1}H NMR δ 0.9 (6 H, d, J = 2 Hz), 1.28 (6 H, d, J = 6 Hz), 1.10–2.10 (6 H, m), and 3.10 (2 H, s). Anal. Calcd for $C_{10}H_{22}O_2$: C, 68.92; H, 12.72. Found: C, 68.79; H, 12.80.

2-Methyl-2,6-heptanediol (25 from 11): 79% yield; bp 113–115 °C (10 mm) [lit.[28] bp 120 °C (12 mm)]; ^{1}H NMR δ 1.18 (3 H, d, J = 6 Hz), 1.20 (6 H, s), 1.46 (6 H, m), 2.18 (2 H, m), and 3.78 (1 H, m).

1-Benzyl-5-methyl-1,5-hexanediol (26 from 12): 88% yield; mp 78–79 °C; ^{1}H NMR δ 1.24 (6 H, s), 1.40–1.80 (8 H, m), 2.80 (2 H, m), 3.90 (1 H, m), and 7.38 (5 H, s). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.73; H, 10.11.

4-Benzyl-4,5-dimethyl-1,5-hexanediol (27 from 13): 71% yield; mp 84–85 °C; ^{1}H NMR δ 0.90 (3 H, s), 1.23 (6 H, s), 1.20–1.72 (6 H, m), 2.70 (2 H, d), 3.46 (2 H, m), and 7.20 (5 H, s). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 75.96; H, 10.15.

2-Methyl-2,7-octanediol (28 from 14): 78% yield; bp 124 °C (0.8 mm); ^{1}H NMR δ 1.20 (3 H, d, J = 6 Hz), 1.22 (6 H, s), 1.44 (8 H, m), 1.90 (2 H, s), and 3.78 (1 H, m). Anal. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.58. Found: C, 67.35; H, 12.70.

3,6-Dimethyl-1,6-heptanediol (29 from 15): 71% yield; bp 120 °C (0.6 mm); ^{1}H NMR δ 0.94 (3 H, d, J = 6 Hz), 1.20–1.80 (7 H, m), 1.84 (2 H, s), and 3.70 (2 H, t, J = 6 Hz). Anal. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.58. Found: C, 67.61; H, 11.73.

2,4,8-Trimethyl-2,7-nonanediol [(±)- and (−)-30 from (±)- and (−)-16]: 70–72% yield; ^{1}H NMR δ 0.84 (6 H, d, J = 6 Hz), 0.98 (3 H, d, J = 6 Hz), 1.22 (6 H, s), 1.20–1.80 (8 H, m), 1.84 (2 H, m), and 3.30 (1 H, m). (−)-**30** showed $[\alpha]^{25}_D$ −14.4° (c 2.2, $CHCl_3$). Anal. [(−)-**30**] Calcd for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95. Found: C, 71.07; H, 12.60.

Enantiomeric Excess Determination Procedure. For the enantiomeric excess measurements, the lactone to diol conversions were performed on a 3–8-mg scale as described above except that the reaction was quenched with water instead of acetic acid.[29] The diol products obtained by evaporation of the ether extracts (quantitative yields) were not purified. They were dissolved directly in carbon tetrachloride, and their NMR spectra were determined at 100 MHz in the presence of up to ~0.4 equiv of Eu(tfc)$_3$. The results are summarized in Table I.

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Registry No.—(±)-**3**, 57129-69-8; (±)-**4**, 69814-97-7; (±)-**5**, 69854-29-1; (±)-**6**, 69814-98-8; (±)-**7**, 61949-75-5; (±)-**8**, 62989-39-3; (±)-**9**, 62948-63-4; (±)-**10**, 21754-22-3; (±)-**11**, 26911-67-3; (±)-**12**, 69814-99-9; (±)-**13**, 69815-00-5; (±)-**14**, 69854-30-4; (±)-**15**, 18951-91-2; **16**, 499-54-7; (±)-**17**, 69854-31-5; (±)-**18**, 69815-01-6; (±)-**19**, 69815-02-7; (±)-**20**, 69815-03-8; (±)-**21**, 69815-04-9; (±)-**22**, 69815-05-0; (±)-**23**, 69815—1; (±)-**24**, 69815-07-2; (±)-**25**, 69815-08-3; (±)-**26**, 69815-09-4; (±)-**27**, 69991-40-8; (±)-**28**, 69815-10-7; (±)-**29**, 69815-11-8; **30**, 69815-12-9; γ-butyrolactone, 96-48-0; benzyl chloride, 100-44-7; 2-benzylcyclopentanone, 69815-13-0; allylbenzylacetic acid, 42361-59-1; 2-benzylpentanoic acid acetone, 68975-21-3; (±)-menthone, 1074-95-9; (−)-menthone, 14073-97-3.

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(15) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Spectral data were as expected for all previously reported compounds. The NMR spectra reported for new compounds were determined in $CHCl_3$ on a Varian T60 instrument. Enantiomeric excess values of diols **17–30** were measured at 100 MHz on CCl_4 solutions using a Varian HA-100 spectrometer. The chiral shift reagent Eu(tfc)$_3$ (Optishift I) was purchased from Willow Brook Laboratories, Waukesha, Wis.
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