was removed in vacuo to provide a slightly green amorphous solid. Analytical TLC (silica gel, 35% ethyl acetate/petroleum ether) indicated the presence of two major bands at R_f = 0.40 and R_f = 0.25. The top band was identified as *N,N,N',N'*-tetraacetylethylenediamine, so the crude mixture was redissolved in dichloromethane (50 mL) and extracted with 3.0 M hydrochloric acid (3 × 25 mL). The combined acid extracts were back-washed with dichloromethane (2 × 50 mL) and then neutralized by the careful addition of a saturated sodium bicarbonate solution. The now slightly basic solution was extracted with dichloromethane (6 × 25 mL), and the combined organic layers were washed with water (2 × 25 mL) and a saturated sodium chloride solution (2 × 25 mL) and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation, and the white solid was subjected to preparative thin-layer chromatography (silica gel, 50% ethyl acetate/petroleum ether). Isolation of the material from the large prominent band at R_f = 0.32 provided 0.21 g (70%) of 1-amino-3,5,7-trinitroadamantane (**2d**). This material was then crystallized slowly from ethyl acetate–hexane to provide colorless needles: mp 200 °C (sealed tube with dec); IR (thin film) 1540 (vs), 1457 (w), 1363 (s), 1232 (w), 734 (w); ^{1}H NMR (acetone-d_6) δ 2.40 (s, 6 H), 2.84 (br s, NH_2), 2.94 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 41.3 (t), 46.7 (t), 52.8 (s), 85.9 (s); mass spectrum (FAB), *m/e* 287 (M + H), 257, 181, 145 (100). Anal. Calcd for $C_{10}H_{14}N_4O_6$: C, 41.96; H, 4.93; N, 19.57. Found: C, 42.44; H, 5.01; N, 19.35.

SPC-TAED/Ozone Oxidation of 1,3,5,7-Tetraaminoadamantane (2a). The tetrahydrochloride of 1,3,5,7-tetraaminoadamantane (**2a**) (0.35 g, 1.0 mmol) was added to a well-stirred biphasic system of ethyl acetate (25 mL) and water (25 mL) containing *N,N,N',N'*-tetraacetylethylenediamine (2.28 g, 10.0 mmol), sodium percarbonate (6.28 g, 40.0 mmol), and sodium bicarbonate (2.30 g, 27.4 mmol). The reaction was stirred for 65 h at room temperature. The blue reaction mixture was transferred to a separatory funnel, and water (100 mL) was added to facilitate the formation of distinct layers. The organic layer was reserved, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with water (2 × 50 mL) and brine (2 × 50 mL) and then dried (anhydrous magnesium sulfate). The drying agent was removed by gravity filtration, and the filtrate was concentrated to a volume of 75 mL. The green solution was cooled to −78 °C and subjected to an ozone–oxygen stream for 1 h. The solvent was removed in vacuo, and the white solid was subjected to preparative thin-layer chromatography (silica gel, 35% ethyl acetate/petroleum ether). The band at R_f = 0.72 was taken and provided 0.29 g (91%) of 1,3,5,7-tetranitroadamantane (**2c**) as ascertained by comparison to an authentic sample. The ^{1}H and ^{13}C NMR spectra were additionally recorded with use of acetone-d_6 in place of dimethyl-d_6 sulfoxide to facilitate sample recovery: mp 348–352 °C (lit.[2a] mp 361–363 °C); ^{1}H NMR (acetone-d_6) δ 3.16 (s, 12 H); ^{13}C NMR (acetone-d_6) δ 41.0 (t), 85.2 (s).

Peroxyacetic Acid/Ozone Oxidation of 1,3,5,7-Tetraaminoadamantane (2a) (pH = 8). The tetrahydrochloride of 1,3,5,7-tetraaminoadamantane (**2a**) (0.35 g, 1.0 mmol) was added to a biphasic mixture of dichloromethane (50 mL), a saturated sodium bicarbonate solution (50 mL), and solid sodium bicarbonate (2.5 g, 29.8 mmol). The peroxyacetic acid solution (4.44 g of a 35% solution, 20.5 mmol, 20 equiv) was added slowly to minimize foaming, and the reaction mixture was stirred vigorously for 3 h at room temperature. The organic layer was separated, and the aqueous phase was washed with dichloromethane (3 × 50 mL). The combined organic layers were washed sequentially with a 1 M sodium hydroxide solution (2 × 100 mL), distilled water (1 × 100 mL), and brine (1 × 100 mL) and dried (anhydrous sodium sulfate). The drying agent was removed by filtration, and the filtrate was reduced to a final volume of 50 mL on a rotary evaporator. The faintly blue solution was cooled (−78 °C) and ozonized for 1 h. The solvent was removed, and the colorless amorphous solid obtained was subjected to preparative thin-layer chromatography (silica gel, chloroform). Isolation of the material from the band at R_f = 0.64 provided 0.28 g (89%) of 1,3,5,7-tetranitroadamantane (**2c**).

Peroxyacetic Acid/Ozone Oxidation of 1,3,5,7-Tetraaminoadamantane (2a) (pH = 11). The procedure used was identical with that of the pH = 8 reaction except that sodium carbonate (7.00 g, 66.0 mmol) was added to the mixture following the addition of the peroxyacetic acid solution to raise the pH of the aqueous layer to ~11. The yield of 1,3,5,7-tetranitroadamantane (**2c**) obtained under these conditions was 0.26 g (84%).

Peroxyacetic Acid Oxidation of 1,3,5,7-Tetraaminoadamantane (2a) (pH = 8). The tetrahydrochloride of 1,3,5,7-tetraaminoadamantane (**2a**) (0.35 g, 1.0 mmol) was added to a mixture of dichloromethane (50 mL), saturated sodium bicarbonate solution, and solid sodium bicarbonate (2.50 g, 29.8 mmol). The peroxyacetic acid solution (4.44 g of a 35% solution, 20.5 mmol, 20 equiv) was slowly added, and the reaction mixture was stirred vigorously for 26 h at room temperature. Additional portions of the peroxyacetic acid solution (4.44 g, 20.5 mmol, 20 equiv) and sodium bicarbonate (5.00 g, 59.5 mmol) were carefully added. The vigorous stirring was continued for 48 h. The organic layer was separated, and the aqueous phase was washed with dichloromethane (3 × 50 mL). The combined organic layers were washed sequentially with a 1 M sodium hydroxide solution (2 × 100 mL) and distilled water (1 × 100 mL) and dried (anhydrous sodium sulfate). The drying agent was removed by filtration, the filtrate was concentrated in vacuo, and the residue was subjected to preparative thin-layer chromatography (silica gel, chloroform). The band at R_f = 0.59 provided 0.23 g (73%) of 1,3,5,7-tetranitroadamantane (**2c**).

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Registry No. **1a**, 768-94-5; **1d**, 7575-82-8; **2a**, 21336-47-0; **2c**, 75476-36-7; **2d**, 119694-48-3; *N,N,N',N'*-tetraacetylethylenediamine, 10543-57-4; sodium percarbonate, 3313-92-6; peroxyacetic acid, 79-21-0.

Synthesis of Enantiomerically Pure γ-(Menthyloxy)butenolides and (*R*)- and (*S*)-2-Methyl-1,4-butanediol

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Chiral butenolides have played a pivotal role in the construction of various natural products.[1] Recently Hanessian and co-workers[2] demonstrated the use of chiral butenolides derived from L-glutamic acid, D-ribonolactone, and D-mannitol as versatile templates for the stereocontrolled synthesis of acyclic structural units containing vicinal or remote substitution patterns. Highly diastereoselective cycloadditions of D-ribonolactone-derived butenolides[3] and related pyranosides[4] have been reported. Enzymatically prepared chiral mono- and bicyclic lactones were elegantly exploited in natural product synthesis.[5]

(1) Scott, J. W. In *Asymmetric Synthesis*; Morrison, J. D., Scott, J. W., Eds.; Academic Press: Orlando, 1984; Vol. 4, Chapter 1. Hanessian, S.; Sahoo, S. P. Botta, M. *Tetrahedron Lett.* **1987**, *28*, 1143. Hanessian, S.; Sahoo, S. P.; Botta, M. *Ibid.* **1987**, *28*, 1147. Ortuño, R. M.; Mercé, R.; Font, J. *Tetrahedron Lett.* **1986**, *27*, 2519. Vigneron, J. P.; Méric, R.; Larchevêque, M.; Debal, A.; Lallemand, J. Y.; Kunesch, G.; Zagatti, P.; Gallois, M. *Tetrahedron* **1984**, *40*, 3521. Fraser-Reid, B.; Anderson, R. C. *Fortschr. Org. Naturstoffe* **1980**, *39*, 1.

(2) Hanessian, S.; Murray, P. J. *J. Org. Chem.* **1987**, *52*, 1170.

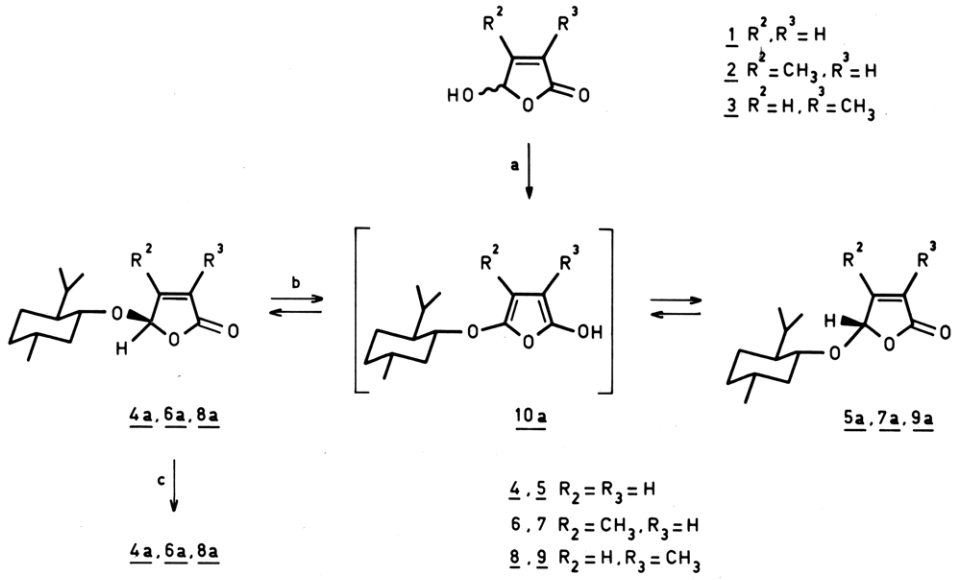
(3) (a) Mann, J.; Thomas, A. *J. Chem. Soc., Chem. Commun.* **1985**, 737. Drew, M. G. B.; Mann, J.; Thomas, A. *J. Chem. Soc., Perkin Trans. 1* **1986**, 2279. (b) Ortuño, R. M.; Corbera, J.; Font, J. *Tetrahedron Lett.* **1986**, *27*, 1081.

(4) Fitzsimmons, B. J.; Fraser-Reid, B. *Tetrahedron* **1984**, *40*, 1279. Rahman, M. A.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1985**, *107*, 5576.

(5) (a) Lok, K. P.; Jakovac, I. J.; Jones, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 2521. (b) Leuenberger, H. G. W.; Boguth, W.; Barner, R.; Schmid, M.; Zell, R. *Helv. Chim. Acta* **1979**, *62*, 455.

0022-3263/89/1954-2471$01.50/0

Scheme I[a]



[a] (a) 1-Menthol, 120 °C; (b) C_6H_6, $CH_3C_6H_5SO_3H$ (0.3%), reflux; (c) crystallization (petroleum ether, 40–60).

Recently we have shown that 5-(*l*-menthyloxy)-2(5*H*)-furanone (**4a**) is an excellent chiral synthon for the preparation of enantiomerically pure amino diols.[6] Furthermore **4a** serves as a chiral maleic anhydride analogue in asymmetric Diels–Alder reactions with virtually complete π-face selectivity with a variety of dienes.[7a]

In view of the expectation that chiral γ-alkoxybutenolides could serve as promising alternatives for carbohydrate-derived chiral butenolides, an efficient route to these synthons is required. We now report the synthesis of enantiomerically pure γ-(menthyloxy)butenolides **4a**, **6a**, and **8a** and butyrolactones **13**, **14**, and **15** as well as the asymmetric synthesis of (*R*)- and (*S*)-2-methyl-1,4-butanediol. 5-(*l*-Menthyloxy)-2(5*H*)-furanone was prepared as a mixture of diastereomers **4a** and **5a** (60:40 ratio)[7b] by heating 5-hydroxy-2(5*H*)-furanone (**1**)[8,9] with 1.5 equiv of *l*-menthol.[10] Enantiomerically pure **4a**[7b] was obtained after two crystallizations of the mixture of **4a** and **5a** from petroleum ether. In a similar way the enantiomer of lactone **4**, with the *S* configuration at the acetal carbon, was obtained starting with *d*-menthol as a chiral auxiliary (Scheme I).[10] The absolute configuration at the acetal carbon of **4a** was proven to be *R* by means of a X-ray structure analysis of its Diels–Alder cycloadduct (**17**) with 2,3-dimethylbutadiene as shown in Figure 1.[11]

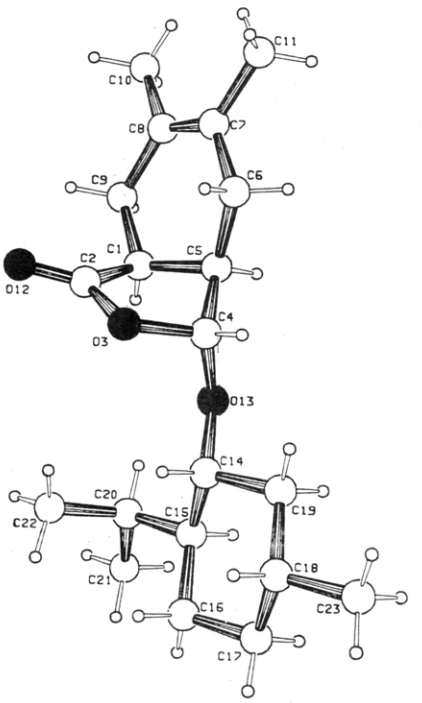
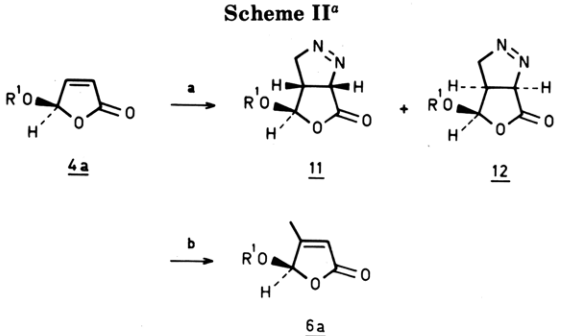


Figure 1. Pluto diagram of the Diels–Alder adduct (**17**) of **4a** and 2,3-dimethylbutadiene.[11]

Scheme II[a]



[a] (a) CH_2N_2, Et_2O; (b) $CH_3C_6H_5$, reflux (R^1O = 1-menthyloxy).

An efficient route (quantitative overall yield) to 5-(*l*-menthyloxy)-4-methyl-2(5*H*)-furanone (**6a**) was developed,

(6) Feringa, B. L.; de Lange, B. *Tetrahedron Lett.* **1988**, *29*, 1303.

(7) (a) Feringa, B. L.; de Jong, J. C. *J. Org. Chem.* **1988**, *53*, 1125. (b) The diastereomeric and enantiomeric purity is readily calculated from the integration of the two well-separated acetal hydrogen absorptions in the ^1H NMR spectra of **4**, **6**, **8** and **5**, **7**, **9**.

(8) Schenk, G. O. *Justus Liebigs Ann. Chem.* **1953**, *584*, 156.

(9) Feringa, B. L. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 469.

(10) Only reactions with *l*-menthol derivatives are pictured in Schemes I–III. In the numbering adopted throughout the text and in the schemes the **a** series denoted *l*-menthol derivatives and the **b** series *d*-menthol derivatives.

(11) Crystal data of **17**: formula $C_{20}H_{32}O_3$; formula weight 320.48 g mol^{-1}; monoclinic; space group *P*2/1; two crystallographically independent molecules, a = 7.365 (1), b = 10.529 (2), and c = 12.256 (1) Å; α = 90.00, β = 97.78, and γ = 90.00°; D_c = 1.130 g cm^{-3}; U = 941.7 (5) Å^3; crystal dimensions 0.15 × 0.32 × 0.50 mm; λ (Mo Kα) = 0.710 73 Å. Data were collected with graphite-monochromated Mo Kα radiation on a CAD4F diffractometer and the structure was solved by direct methods. A total of 2269 unique reflections with $I > 3.0\sigma(I)$ were used in full-matrix least-squares refinement, including H atoms with isotropic thermal parameters, to R = 0.051, R_w = 0.064. No. of unobservedly weak refections, 11. No significant features on a final difference Fourier map. Bond lengths and angles as expected were found (see the supplementary material).

starting with enantiomerically pure butenolide **4a**.[12] Treatment of **4a** with excess diazomethane[13] afforded pyrazolines **11** and **12** as a mixture of two diastereoisomers (60:40 ratio) (Scheme II). ^{1}H NMR data and thermolysis of the mixture of **11** and **12** to a single product (vide infra) indicate that the formation of two isomers of **11** and **12** is the result of low π-face selectivity and that it is not due to low regioselectivity in the cycloaddition step.

The trans configuration with respect to the menthyloxy substituent and the pyrazoline ring was assigned to the major isomer **11**. This assignment is based on the coupling constant ($J_{3a,4}$ = 6.0 Hz)[14] for the vicinal hydrogens at the C_{3a} and C_4 chiral centers of the cis isomer **12**, whereas for the trans isomer a singlet was observed for the acetal hydrogen.

In contrast to our results the addition of diazopropane to 5-alkyl-substituted butenolides proceeds diastereoselectively but with low regioselectivity.[3a,15]

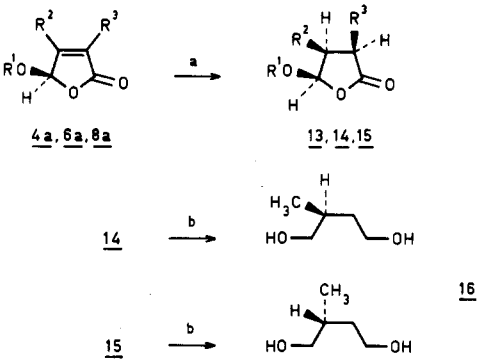
The observed change in regioselectivity has ample precedent in the cycloaddition of diazoalkanes to substituted methylacrylates.[16] Furthermore low diastereoselectivity has been reported in the addition reactions of diazo compounds to ethylcinnamate and related systems.[16,17]

Enantiomerically pure butenolide **6a**[7b] was obtained quantitatively by thermolysis of the mixture of **11** and **12** in toluene. A similar route from enantiomerically pure 5-(*d*-menthyloxy)-2(5*H*)-furanone (**4b**) provided the enantiomer **6b**.

In an alternative route to **6b** 5-hydroxy-4-methyl-2-(5*H*)-furanone[18] (**2**) was treated with *d*-menthol followed by crystallization of the mixture of diastereoisomers of **6b** and **7b** (Scheme I).[10] The overall yield (36%) of enantiomerically pure **6b** is, however, lower than via the diazomethane route.[19]

3-Methyl-2-furoic acid[20] served as the starting material for 5-(*l*-menthyloxy)-3-methyl-2(5*H*)-furanone (**8a**). Photooxidation[9] of 3-methyl-2-furoic acid to 5-hydroxy-3-methyl-2(5*H*)-furanone (**3**) followed by acetalization with *l*-menthol and subsequently crystallization yielded **8a** as a single enantiomer.[7b] A remarkable epimerization[7,21,22] of **4–9** accompanies the above described crystallization processes to provide approximately constant ratios of epimers in solution (Scheme I). This epimerization reaction can be accelerated by brief heating of the mother liquor in the presence of catalytic amounts of *p*-toluenesulfonic acid. The conversion of the "wrong" diastereoisomers **5a**, **7a**, and **9a** presumably proceeds via enolization to the unstable 2-hydroxyfuran intermediate **10a**, which is achiral except for the *l*-menthyl moiety. This epimerization facilitates the formation of enantiomerically pure lactones **4a**, **6a**, and **8a** drastically as is demonstrated by the isolation of **8a** in 78% yield.

Scheme III[a]



[a] (a) H_2, 10% Pd/C, EtOAc; (b) $LiAlH_4$, THF (R^1O = 1-menthyloxy).

Hydrogenation of butenolides **4a**, **6a**, and **8a** proceeds with complete stereocontrol to give enantiomerically pure lactones **13**, **14**, and **15** (Scheme III). A single isomer was observed in the ^{1}H NMR and ^{13}C NMR spectra of the hydrogenation products. The cis relationship of the methyl substituents at the 4- and 3-positions in **14** and **15** and the menthyloxy substituent was deduced from ^{1}H NMR coupling constants (see the Experimental Section)[14] and chemical correlation. For **14** a doublet at δ 5.43 ppm with J = 5.0 Hz was observed for C_{5-H} indicating the cis C_4–C_5 relationship.[14] Futhermore lithium aluminum hydride reduction of **14** gives (*S*)-2-methyl-1,4-butanediol ((*S*)-**16**) whereas reduction of **15** results in the formation of (*R*)-**16**.[23] These chemical correlations together with the established configuration at the acetal center of **4a** via X-ray analysis unequivocally established the absolute configuration at the C_3 and C_4 centers in **15** and **14**, respectively. As the optical rotations of (*R*)- and (*S*)-**16** did not provide conclusive evidence of the enantiomeric purity[26] and in order to exclude any epimerization at the acetal center during the conversions, an unambiguous proof of the enantiomeric excess (ee) was necessary. Chromatography of the dibenzoates of **16** on a chiral stationary phase (see the Experimental Section) showed exclusively one enantiomer for the products of the asymmetric synthesis resulting in an ee > 98% for both the dibenzoates of (*R*)- and (*S*)-**16**.

It is noteworthy to mention that both enantiomers of **16** are obtained by using the same enantiomer of the chiral auxiliary *l*-menthol. Sequential elaboration at the acetal or the lactone functionalities in **14** and **15** allows formation of both enantiomers of isopentane building blocks from the same precursor.

The asymmetric synthesis of **16** demonstrated only one of the many applications that can be foreseen with chiral γ-alkoxybutenolides. Furthermore it provides a practical alternative for reported routes to **16** based on methylsuccinic acid.[23,27] Compounds **4**, **6**, **8**, and **13–15** might be

(12) The absolute configuration at the acetal carbon of **6a** was determined to be *R* via its formation from **4a** without affecting the acetal carbon center (Scheme II). The absolute configuration of **6a** and **8a** were correlated via the route depicted in Scheme III providing (*S*)- and (*R*)-**16**, respectively.

(13) Fariña, F.; Martín, M. V.; Sánchez, F. *Heterocycles* **1986**, *24*, 2587.

(14) Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; de Leeuw, H. P. M.; Altona, C. *Org. Magn. Reson.* **1981**, *15*, 43. For adopted numbering, see the Experimental Section. The cis and trans isomers of 4-substituted 5-alkoxybutyrolactones could be distinguished readily in all cases we have studied so far[6,7] on the basis of a small (J < 2 Hz) or no proton coupling for the C_5 acetal hydrogen for the trans isomer and a 5–8-Hz coupling for the cis isomer.

(15) Franck-Neumann, M.; Sedrati, M.; Vigneron, J. P.; Bloy, V. *Angew. Chem.* **1985**, *97*, 995; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 996.

(16) For an excellent review, see: Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, Chapter 1.

(17) Unfortunately the stereochemical result of recently reported diazomethane additions to ribonolactone derived 5-alkylbutenolides was not indicated. Ortuño, R. M.; Bigorra, J.; Font, J. *Tetrahedron* **1987**, *43*, 2199.

(18) Bourguignon, J. J.; Wermuth, C. G. *J. Org. Chem.* **1981**, *46*, 4889.

(19) The enantiomer **6a** was obtained via a similar procedure starting with *l*-menthol.

(20) Burness, D. M. *Org. Synth.* **1959**, *39*, 46 and 49.

(21) For related crystallization-induced asymmetric transformation, see: Jacquet, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley: New York, 1981; p 369. Reider, P. J.; Davis, P.; Hughes, D. L.; Grabowski, E. J. J. *J. Org. Chem.* **1987**, *52*, 957.

(22) Martel, J.; Tessier, J.; Demoute, J. P. Eur. Pat. Appl. 23 454, 1981; *Chem. Abstr.* **1981**, *95*, 24788.

(23) Kaneko, T.; Katsura, H.; Asano, H.; Wakabayashi, K. *Chem. Ind.* **1960**, 1187. See also: Von Braun, J. V.; Jostes, F. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 1444.

exploited as C_4 and C_5 synthons, taking advantage of the dual functionality present and the high stereocontrol[6,7a] in their conversions observed so far.

Experimental Section[24]

Preparation of Butenolides 4–9. 5-Hydroxy-2(5*H*)-furanones **1**, **2**, and **3** (40.8 mmol) were heated at 120 °C during 3 days with *d*- or *l*-menthol (6.69–9.54 g, 42.9–61.2 mmol). The excess menthol was removed by bulb-to-bulb distillation at 80 °C (0.1 mm). The butenolides **4–9** (oils, mixtures of diastereoisomers) were obtained by distillation at reduced pressure; bp range 120–150 °C (0.1 mm). Compounds **4–9** solidified upon prolonged standing. 5-(*l*-Menthyloxy)-2(5*H*)-furanone (**4a + 5a**): yield 61%; ratio of diastereoisomers 60:40. 5-(*d*-Menthyloxy)-3-methyl-2(5*H*)-furanone (**8b + 9b**): yield 6.58 g (64%); ratio of diastereoisomers 60:40. 5-(*l*-Menthyloxy)-4-methyl-2(5*H*)-furanone (**6a + 7a**): yield 6.07 g (59%); ratio of diastereoisomers 70:30.

General Procedure for the Crystallization and Epimerization of Butenolides 4–9. A mixture of diastereoisomers of 5-(*l*-menthyloxy)-3-methyl-2(5*H*)-furanone (**8a + 9a**) (21.6 g, 85.5 mmol) was dissolved in petroleum ether (40–60) (100 mL) and subsequently cooled to −18 °C. The white crystalline material was collected and recrystallized once from 50 mL of petroleum ether (40–60) to afford 8.12 g of enantiomerically pure **8a**. The combined mother liquors were evaporated to dryness. The remaining solid was redissolved in benzene and heated at reflux in the presence of a catalytic amount (0.3 mol %) of *p*-toluenesulfonic acid during 1 h. The solvent was removed in vacuo, and the residue was crystallized from petroleum ether (40–60) to afford enantiomerically pure **8a** (7.0 g). This procedure was repeated a second time to give 16.8 g (78% combined yield) of enantiomerically pure **8a**.

Crystallization of 7.0 g of 5-(*d*-menthyloxy)-4-methyl-2(5*H*)-furanone (**6b + 7b**) yielded 2.5 g (36%) of enantiomerically pure **6b** prior to epimerization as described above. Crystallization of 7.25 g of 5-(*l*-menthyloxy)-2(5*H*)-furanone (**4a + 5a**) yielded 3.12 g (43%) of enantiomerically pure **4a** prior to epimerization. Combined yield after epimerization, 60%.

4a: bp 120–123 °C (0.01 mmHg); mp 70.5–70.7 °C; $[\alpha]^{20}_D$ −136.4° (*c* 1.0, 95% EtOH); ^{1}H NMR ($CDCl_3$, 60 MHz, ppm) 0.65–2.32 (m, 18 H, menthyl H's), 3.58 (m, 1 H, CHO), 5.97 (s, 1 H, C_5-H), 6.10 (d, 1 H, J = 6.0 Hz, C_3-H), 7.08 (d, 1 H, J = 6.0 Hz, C_4-H); ^{13}C NMR ($CDCl_3$, ppm) 15.51 (q), 20.57 (q), 21.93 (q), 22.87 (t), 25.04 (d), 31.17 (d), 33.93 (t), 40.05 (t), 47.46 (d), 78.79 (d), 100.26 (d), 124.36 (d), 150.79 (d), 170.46 (s); HRMS calcd 238.157, found 238.155. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.49; H, 9.18.

6a: mp 88.8–90.0 °C; $[\alpha]^{20}_D$ −130.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 0.70–1.90 (m, 18 H, menthyl H's), 2.08 (s, 3 H, CH_3), 3.65 (m, 1 H, CHO), 5.72 (s, 1 H, C_5-H), 5.81 (s, 1 H, C_3-H); ^{13}C NMR ($CDCl_3$, ppm) 13.17 (q), 15.49 (q), 20.75 (q), 22.09 (q), 22.94 (t), 25.08 (d), 31.28 (d), 34.05 (t), 40.24 (t), 47.58 (d), 79.25 (d), 101.52 (d), 118.62 (d), 163.69 (s), 171.01 (s); IR (KBr) λ_{max} 2950, 1790 cm^{-1}; HRMS calcd 252.173, found 252.174. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.35; H, 9.58. Found: C, 71.23; H, 9.50.

8a: mp 93.4–94.1 °C; $[\alpha]^{20}_D$ −132.4° (*c* 1.0, *n*-hexane); ^{1}H NMR ($CDCl_3$, 60 MHz, ppm) 0.58–2.43 (m, 21 H, menthyl H's + CH_3), 3.57 (m, 1 H, CHO), 5.84 (s, 1 H, C_5-H), 6.68 (s, 1 H, C_4-H); ^{13}C NMR ($CDCl_3$, ppm) 10.42 (q), 15.59 (q), 20.72 (q), 22.03 (q), 22.97 (t), 25.11 (d), 31.31 (d), 34.07 (t), 40.30 (t), 47.63 (d), 78.62 (d), 98.56 (d), 133.50 (s), 143.34 (d), 171.87 (s); HRMS calcd 252.173, found 252.172. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.35; H, 9.58. Found: C, 71.11; H, 9.67.

4-(*l*-Menthyloxy)-3,3a,4,6a-tetrahydro-6*H*-furo[4,5-*c*]-pyrazol-6-one (11 + 12). To a solution of 1.5 g (6.3 mmol) of 5-(*l*-menthyloxy)-2(5*H*)-furanone (**4a**) in 40 mL of ether stirred at −10 °C was added 10.0 mmol of diazomethane in ether. The mixture was stirred at −10 °C for 0.5 h and subsequently at room temperature for 10 h protected from light. The ether was evaporated to afford 1.78 g (100%) of pure adduct (60:40 mixture of diastereoisomers **11** + **12**) as a slight yellow powder: mp 112–118 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 0.74–2.08 (m, 18 H, menthyl H's **11**, **12**), 2.80 (m, 0.6 H, C_{3a}-H, **11**), 3.12 (m, 0.4 H, C_{3a}-H, **12**), 3.54 (m, 1.0 H, CHO, **11**, **12**), 4.40 (dd, 0.4 H, J = 8.0, 15.0 Hz, C_3-H, **12**), 4.76 (dd, 0.6 H, J = 1.0, 15.0 Hz, C_3-H, **11**), 5.04 (dd, 0.6 H, J = 8.0, 15.0 Hz, C_3-H, **11**), 5.38 (s, 0.6 H, C_4-H, **11**), 5.45 (dd, 0.4 H, J = 1.0, 15.0 Hz, C_3-H, **12**), 5.57 (d, 0.4 H, J = 8.0 Hz, C_{6a}-H, **12**), 5.71 (d, 0.4 H, J = 6.0 Hz, C_4-H, **12**), 5.81 (d, 0.6 H, J = 8.0 Hz, C_{6a}-H, **11**); ^{13}C NMR ($CDCl_3$, ppm) 15.51 (q), 20.82 (q), 22.13 (q), 22.94 (t), 25.35 (d), 31.21 (d), 34.08 (t), 39.27 (t), 39.58 (t), 47.57 (d), 77.62 (d), 83.43 (t), 93.14 (d), 104.28 (d), 166.92 (s); IR (KBr) λ_{max} 2950, 1760, 1580, 1200 cm^{-1}; HRMS ($M^+ - N_2$) calcd 252.173, found 252.172.

5-(*l*-Menthyloxy)-4-methyl-2(5*H*)-furanone (6a). A solution of 1.78 g (6.3 mmol) of the mixture of **11** and **12** in 30 mL of toluene was heated at reflux for 12 h. The solution was evaporated to dryness to afford 1.6 g (6.3 mmol, 100%) of enantiomerically pure **6a**: mp 88.8–90.0 °C; $[\alpha]^{23}_D$ −130.0° (*c* 1.0, $CHCl_3$); HRMS calcd 252.173, found 252.174.

Hydrogenation of Butenolides 4, 6, and 8. In a typical experiment 3.9 mmol of butenolide was dissolved in 25 mL of ethyl acetate. After addition of 2 mL of triethylamine and 0.1 g of 10% Pd/C the mixture was hydrogenated in a Parr apparatus (40 psi of H_2) at room temperature over 12.5 h. After filtration over Celite the solvent was removed in vacuo to afford pure butyrolactones **13–15**.

(−)-**13**: white crystals, 0.88 g (3.7 mmol, 94%); mp 57.6–58.9 °C (petroleum ether, 40–60); $[\alpha]^{20}_D$ −178.4° (*c* 1.0, *n*-hexane); ^{1}H NMR ($CDCl_3$, 60 MHz, ppm) 0.65–2.77 (m, 22 H, menthyl H's, 2 CH_2), 3.51 (m, 1 H, CHO), 5.70 (d, 1 H, J = 4 Hz, C_5-H); ^{13}C NMR ($CDCl_3$, ppm) 15.23 (q), 20.52 (q), 21.86 (q), 22.73 (t), 25.06 (d), 26.65 (t), 28.73 (t), 30.96 (d), 33.95 (t), 39.42 (t), 47.37 (d), 76.14 (d), 100.02 (d), 176.20 (s); HRMS calcd 240.173, found 240.174. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 69.79; H, 10.04.

(−)-**14**: oil, 0.89 g (3.51 mmol, 90%); bp 130 °C (0.15 mm); $[\alpha]^{20}_D$ −172.4° (*c* 1.0, *n*-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 0.66–0.96 (m, 12 H), 1.04 (d, 3 H, J = 7.0 Hz), 1.15 (m, 1 H), 1.30 (m, 1 H), 1.57 (m, 2 H), 1.96 (m, 2 H), 2.23 (m, 1 H), 2.36–2.55 (m, 2 H), 3.40 (dt, 1 H, J = 5.0, 11.0 Hz), 5.43 (d, 1 H, J = 5.0 Hz); ^{13}C NMR ($CDCl_3$, ppm) 12.75 (q), 15.48 (q), 20.66 (q), 22.05 (q), 22.98 (t), 25.38 (d), 31.10 (d), 34.13 (t), 34.39 (t), 35.03 (d), 39.57 (t), 47.53 (d), 76.23 (d), 101.60 (d), 176.52 (s). HRMS calcd 254.188, found 254.189. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.65; H, 10.23.

(+)-**14**: yield 98%; bp 130–135 °C (0.1 mm); $[\alpha]^{20}_D$ +167.3° (*c* 1.0, *n*-hexane).

(−)-**15**: white crystals, 0.84 g (3.31 mmol, 83%); mp 104.5–106.8 °C; $[\alpha]^{20}_D$ −177.0° (*c* 1.0, *n*-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) 0.76–1.08 (m, 12 H), 1.23 (m, 1 H), 1.36 (m, 1 H, + d, 3 H, J = 7 Hz), 1.65 (m, 2 H), 1.78 (m, 1 H), 2.11 (m, 2 H), 2.58 (m, 2 H), 3.53 (dt, 1 H, J = 5.0, 11.0 Hz), 5.65 (dd, 1 H, J = 4.3, 5.7 Hz); ^{13}C NMR ($CDCl_3$, ppm) 15.36 (q), 16.50 (q), 20.78 (q), 22.07 (q), 22.79 (t), 25.21 (d), 31.20 (d), 34.14 (t), 34.41 (d), 36.55 (t), 39.64 (t), 47.56 (d), 77.33 (d), 99.29 (d), 178.69 (s). HRMS calcd 254.188, found 254.189. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.60; H, 10.34.

(*R*)-2-Methylbutane-1,4-diol ((*R*)-16). To a stirred suspension of 0.21 g (5.6 mmol) lithium aluminum hydride in 50 mL of tetrahydrofuran at 0 °C under an inert atmosphere of nitrogen was added a solution of 0.70 g (2.8 mmol) of (−)-**15** in 10 mL of tetrahydrofuran. The solution was stirred at 0 °C for 30 min and subsequently at room temperature for 12 h. The excess lithium aluminum hydride was destroyed by adding carefully 2 mL of H_2O. The resulting mixture was filtered, the organic solvent was re-

(24) NMR spectra were obtained at 300 or 75.43 MHz in deuteriochloroform solution. Melting points are uncorrected. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. All other solvents were distilled before use. Et_3N was dried over KOH. *d*- and *l*-Menthol were purchased from Janssen Chimica. 3-Methyl-2-furoic acid was prepared via the procedure described by Burness.[20] 5-Hydroxy-4-methyl-2(5*H*)-furanone was prepared as reported. Photooxidations of furfural and 3-methyl-2-furoic acid were performed with rose bengal or methylene blue as sensitizer and a 700-Watt high-pressure mercury lamp (Hanau) via the procedures described before.[9,25]

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moved in vacuo, and water (30 mL) was added to the residue obtained. This mixture was extracted with *n*-hexane (3 × 50 mL) to remove the *l*-menthol. The water layer was subsequently concentrated in vacuo, and the residue was dissolved in CH_2Cl_2 (50 mL). Finally the solution was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to afford 0.29 g (100%) of pure (*R*)-(+)-**16** as a colorless oil: Kugelrohr distillation yielded 0.25 g (87%) (*R*)-(+)-**16** (bp 130 °C/15 mmHg; lit.[26] bp 132 °C/18 mmHg); $[\alpha]^{20}_D$ +13.2° (*c* 1.0, MeOH); $[\alpha]^{20}_D$ +13.6° (*c* 3.3, MeOH); (*S*)-(−)-**16** (lit.[26] $[\alpha]^{20}_D$ −14.4° (*c* 0.6, MeOH)); ^{1}H NMR ($CDCl_3$, ppm) 0.92 (d, 3 H, *J* = 6 Hz), 1.50–1.62 (m, 2 H), 1.70 (m, 1 H), 3.42–3.84 (m, 4 H), 4.20 (br s, 2 H); ^{13}C NMR ($CDCl_3$, ppm) 17.06 (q), 33.77 (d), 37.20 (t), 60.53 (t), 67.77 (t).

(*R*)-(+)-**16** obtained from (+)-**14** via this procedure: $[\alpha]^{20}_D$ +13.4° (*c* 0.6, MeOH). (*S*)-(−)-**16** obtained from (−)-**14** via this procedure: $[\alpha]^{20}_D$ −13.1° (*c* 3.3, MeOH). Further spectral data of (*R*)- and (*S*)-**16** were identical with those reported.[26]

(*R*)-2-Methylbutane-1,4-diol Dibenzoate ((*R*)-18). To a solution of 0.50 g (4.8 mmol) of (*R*)-**16** in 10 mL of dry pyridine was added 1.35 g (9.6 mmol) of benzoyl chloride. This mixture was heated at reflux for 6 h. After the mixture was cooled to room temperature, ether (50 mL) was added, and the solution was washed with saturated aqueous ammonium chloride (2 × 50 mL) and water (50 mL) and subsequently concentrated in vacuo. The yellow residue was purified by Kugelrohr distillation to afford 1.3 g (88%) of (*R*)-2-methylbutane-1,4-diol dibenzoate as a colorless oil: bp 190 °C (0.1 mmHg); $[\alpha]^{20}_{589}$ −9.5° (*c* 2.0, $CHCl_3$).

(*S*)-2-Methylbutane-1,4-diol Dibenzoate ((*S*)-18): $[\alpha]^{20}_{589}$ +9.4° (*c* 2.0, $CHCl_3$). (*R,S*)-2-Methylbutane-1,4-diol dibenzoate was prepared similarly from (*R,S*)-2-methylbutane-1,4-diol (bp 132 °C/15 mmHg):[27] IR (neat) 3100, 2900, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$, ppm) 0.95 (d, 3 H, *J* = 8 Hz), 1.44–1.62 (m, 1 H), 1.79–1.91 (m, 1 H), 1.97–2.10 (m, 1 H), 4.08 (d, 2 H, *J* = 6 Hz), 4.21–4.36 (m, 2 H), 7.19–7.91 (m, 10 H); ^{13}C NMR $CDCl_3$, ppm) 16.60 (q), 29.91 (d), 32.20 (t), 62.66 (t), 69.07 (t), 128.08 (d), 129.22 (d), 129.93 (d), 132.61 (d), 166.15 (s).

Enantiomeric Excess Determination. (*R,S*)-2-Methylbutane-1,4-diol dibenzoate was separated into its enantiomers by HPLC on a Chiracel OB (Daicel) column using 2-propanol/*n*-hexane (5:95) as the eluents. The dibenzoates from (*R*)- and (*S*)-**16**, prepared via the routes outlined above, were single enantiomers with different retention times indicating an enantiomeric excess ≥98%. The minor enantiomer of artificial mixtures of either (*R*)- or (*S*)-**18** with <5% of its antipode was readily detected.

Supplementary Material Available: Tables of final atomic positional parameters, atomic thermal parameters, and bond distances and angles from the X-ray determination of **17** (7 pages). Ordering information is given on any current masthead page.

Electroorganic Synthesis Using Organometals. 1. Cathodic Ester Formation from Alcohols and Alkyl Halides in the Presence of Catalytic Amounts of Iron(0) Pentacarbonyl at Atmospheric Pressure of Carbon Monoxide

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Electrochemical reactions of carbon monoxide are interesting from the aspect of C_1 electrochemistry and provide new synthetic routes to useful organic compounds.[1] However, carbon monoxide must be used at high pressures of 10 to >100 atmospheres in most cases, since its solubility in solvents used for the electrolytic solutions is generally low. This is a very serious problem not only in designing practical cells but also in performing electrolysis. Yet, Cipris[2] reported that satisfactory results in the formation of methyl formate and *N*-alkylformamides could be obtained by cathodically reducing methanol to methoxide ion in the absence and presence of amines, respectively, at ca. 100 atm of carbon monoxide pressure. Equivalent reactions would be also performed by using bases other than the electrogenerated methoxide ion.

It is well-known that the troublesome use of high pressures can be avoided by using transition metal carbonyls and carbon monoxide at atmospheric pressure.[3]

For example, Tustin and Hembre[4] reported the formation of methyl benzoate (22–68% yield) and methyl benzyl ether (5–38%) from the reaction of benzyl halides with potassium carbonate, iron(0) pentacarbonyl, and carbon monoxide at atmospheric pressure and room temperature in methanol [Scheme I ($Q^+ = K^+$)].

There has been an increasing interest in the utilization of anionic species with onium counterions in organic synthesis, since their reactivities are sometimes quite different from those of the same kind of anions with alkali metal counterions.[5] However, the preparation of the anionic species with onium counterions from the corresponding

Scheme I

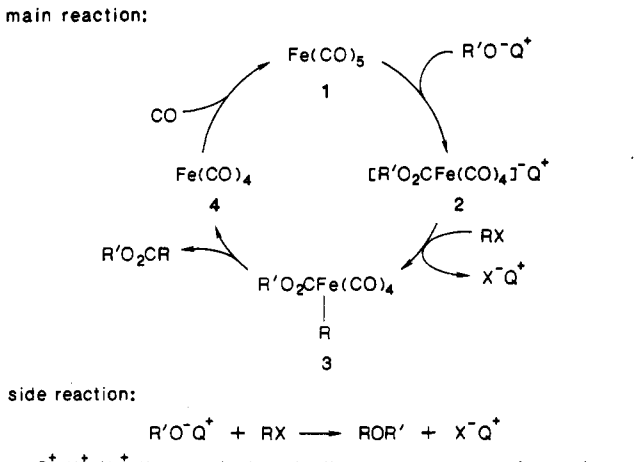

Table I. Reaction of Electrogenerated Methoxide Ion Having Tetramethylammonium Counterion with Benzyl Bromide and Various Amounts of Iron(0) Pentacarbonyl under a Nitrogen Atmosphere

$Fe(CO)_5$, equiv[a]	methyl phenylacetate yield, %
0.05	16
0.1	32
0.2	56
0.5	92
1.0	93

[a] To benzyl bromide used.

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