

molecule has but one carbonyl group which accepts hydrogen bonds from two different host molecules. Stacking interactions between the tropolone ring and the phenyl rings of the host molecules seem to be very important in this structure (see Figure 2).

**Enantioselectivity.** The guest molecules **2** and **3** undergo different photochemical reactions; **2** undergoes photochemical electrocyclic ring closure (see Scheme 1) while **3** undergoes H abstraction followed by ring closure. Tropolone ethyl ether undergoes a disrotatory closure either through path A or through path B (see Scheme 1) to form (-)-**4** or (+)-**4**, respectively. It seems that the enantioselectivity is controlled by the ethyl ether substituent. Mean plane calculation through the tropolone moiety shows that atoms O(4), C(38), and C(39) [see atomic notation in **2**] are displaced by 0.11, 0.19, and 0.31 Å, respectively, from this plane. The direction of the displacement is consistent with path A.

The enantioselectivity of **3** is controlled by the conformation about the O=C—C=O single bond. The observed torsion angle is 101° and in the absence of a mirror symmetry related molecule (torsion angle of -101°), a single enantiomer is formed.

### Conclusions

Systematic study of related compounds is needed to prove that the enantioselectivity is governed by the conformation of the photochemical reactive species and by the space provided by the molecular packing. It is clear, however that the chiral host molecule holds the guest in a specific conformation (as at the active site of an enzyme) and hence that the chirality of the product is dictated by the chirality of the host.

### Experimental Section

The preparation and the photolysis of the inclusion compounds **1-2** are described in ref 1 and 4.

**Preparation of a 1:1 Complex of (-)-1 and 3.** When a solution of (-)-**1** (1.0 g, 2.1 mmol) and **3** (0.37 g, 2.1 mmol) in ether-petroleum ether (1:1) (10 mL) was kept at room temperature for a day, a 1:1 complex of (-)-**1** and **3** was obtained as colorless prisms (1.02 g, 74.5%; mp 126-127 °C. Found: C, 72.8; H, 4.87; N, 2.21. Calcd for C<sub>40</sub>H<sub>31</sub>NO<sub>4</sub>Cl<sub>2</sub>: C, 72.73; H, 4.73; N, 2.12.

**Photoreaction of a 1:1 Complex of (-)-1 and 3 in the Solid State.** The powdered 1:1 complex (0.85 g) of (-)-**1** and **3** was irradiated by a 400-W high-pressure Hg lamp at room temperature, for 27 h with occasional grinding with a pestle and mortar. The reaction mixture was chromatographed on silica gel with benzene-ethyl acetate as solvent to give (-)-**1** (1.0 g, 100%) and 100% ee (-)-**5** (optical purity was determined by HPLC on Chiralcel OC (Daicel Chemical Ind.), [α]<sub>D</sub> -99.7° (c 0.34, CHCl<sub>3</sub>) as colorless plates, mp 123-124 °C. Found: C, 67.66; H, 6.28; N, 7.76. Calcd for C<sub>10</sub>H<sub>11</sub>NO<sub>2</sub>: C, 67.78; H, 6.26; N, 7.91.

Other details of analysis of the photolysis products of similar systems are described in ref 4.

**Crystal Data.** 6-Bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol-tropolone ethyl ether [C<sub>30</sub>H<sub>20</sub>O<sub>2</sub>Cl<sub>2</sub>-C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>; **1-2**], orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 26.446 (12) Å, *b* = 14.328 (7) Å, *c* = 8.679 (4) Å. The calculated density is 1.279 g/cm<sup>3</sup> for *Z* = 4. At the end of the refinement of 2185 reflexions [*F*<sub>o</sub> > 1.5σ(*F*<sub>o</sub>)] the agreement factors are *R* = 0.065 and *R*<sub>w</sub> = 0.054 (*w* = 2.4311/[σ(*F*<sub>o</sub>)<sup>2</sup> + 0.003*F*<sub>o</sub><sup>2</sup>]).

1,6-Bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol-*N,N*-dimethyl- $\alpha$ -oxobenzeneacetamide [C<sub>30</sub>H<sub>20</sub>O<sub>2</sub>Cl<sub>2</sub>-C<sub>10</sub>H<sub>11</sub>NO<sub>2</sub>; **1-3**], orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 26.656 (12) Å, *b* = 15.458 (8) Å, *c* = 8.129 (4) Å. The calculated density is 1.310 g/cm<sup>3</sup> for *Z* = 4. At the end of the refinement of 2222 reflexions [*F*<sub>o</sub> > 1.5σ(*F*<sub>o</sub>)] the agreement factors are *R* = 0.065 and *R*<sub>w</sub> = 0.054 (*w* = 0.9865/[σ(*F*<sub>o</sub>)<sup>2</sup> + 0.0*F*<sub>o</sub><sup>2</sup>]). Intensity data were collected on a PW 1100 four-circle diffractometer using  $\omega$ -2 $\theta$  scans and graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.7107 Å). Both structures were solved by MULTAN 80<sup>20</sup> and refined by SHELX<sup>21</sup>

in two separate blocks consisting of the host molecule in one and the guest and hydrogen atoms in the other. The correct enantiomorph was introduced according to the preparation procedure.<sup>6,4</sup> (For supplementary material see paragraph at the end of the paper).

**Acknowledgment.** This work was partially supported in Israel by the Fund for Promotion of Research at the Technion—Israel Institute of Technology.

**Registry No.** (S)-(-)-**1-2**, 107932-02-5; (S)-(-)-**1-3**, 115118-99-5; (S)-(-)-**5**, 115119-00-1.

**Supplementary Material Available:** Tables of atomic coordinates, isotropic and anisotropic atomic displacement parameters, and bond lengths and angles (14 pages); tables of structure factors (26 pages). Ordering information is given on any current masthead page.

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### Alkylation of (1*S*,2*R*,5*R*,6*S*,7*R*)- and (1*R*,2*R*,5*R*,6*S*,7*S*)-5-Methyl-4-oxatricyclo-[5.2.1.0<sup>2,6</sup>]-8-decen-3-one. Application to the Synthesis of (*R*)-3-Alkyl-5-methyl-2(5*H*)-furanones

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Received January 29, 1988

The retro-Diels-Alder reaction has been extensively applied for the synthesis of natural products in the last 10 years.<sup>1</sup> In one of the most frequent synthetic strategies, this reaction is used to protect a double bond, generated again after elimination of the diene. We have recently reported the Diels-Alder cycloaddition of (*R*)-angelica lactone, **1**,<sup>2</sup> with cyclopentadiene to afford enantiomerically pure endo and exo adducts, **2** and **3**, respectively.<sup>3</sup> In the present work, we describe the alkylation of both diastereoisomeric adducts and subsequent pyrolysis to provide an easy entry to optically active (*R*)-3-alkyl-5-methyl-2(5*H*)-furanones **12-15** in good yields. Many of such compounds have a natural origin and interesting properties, e.g., butenolide **12** is a component of mushroom flavor,<sup>4</sup> **13** has fungicidal activity,<sup>5</sup> and **14** is a metabolite from *Streptomyces griseus*.<sup>6</sup> A related route has been published,<sup>7</sup> based on the alkylation of adducts from maleic anhydride and cyclopentadiene, to yield racemic butenolides. On the other hand, the method reported herein provides a general pathway leading to a variety of dialkyl

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Table I. Pyrolysis of the Alkylated Adducts 4-11

R <sup>a</sup>	temp, <sup>b</sup> °C		time, days		butenolide	% yield <sup>c</sup>		[α] <sub>D</sub> <sup>20</sup> <sup>d</sup>	
	endo	exo	endo	exo		from endo	from exo	from endo	from exo
Me	285	285	4	6	12	88	89	-80.7	-80.5
Et	285	285	2	5	13	87	86	-74.0	-74.7
Bu	240	240	3.5	5	14	80	60	-53.5	-53.7
PhCH <sub>2</sub>	285	285	2	5	15	99	83	-24.8	-24.3

<sup>a</sup> Pyrolysis was performed in benzene solutions, but for R = Bu in toluene. <sup>b</sup> In a ±5-deg interval. <sup>c</sup> Isolated yields. <sup>d</sup> In CHCl<sub>3</sub>.

α,β-butenolides in a single enantiomeric form, since the starting optically active 5-alkyl-2(5*H*)-furanones are easily available.<sup>8</sup>

The procedure used is outlined in Scheme I. Exo-adduct 3 exhibited lower reactivity than endo-adduct 2 in the alkylation process. Thus, while the enolate derived from endo-isomer 2 reacted with 2 equiv of methyl iodide at -78 °C giving compound 4 in quantitative yield, exo-isomer 3 remained unaltered under identical conditions. In contrast, compound 3 when treated with 2 equiv of LDA at -78 °C, followed by D<sub>2</sub>O quenching, incorporated deuterium at C-2 in over 80% (<sup>1</sup>H NMR), thus showing that the C-2 anion was indeed formed. Finally, it was successfully reacted with a large excess of MeI, affording alkylated product 5 in 92% yield. In the same way, alkylation reactions were performed on both adducts 2 and 3, using 10–20 equiv of ethyl-, butyl-, and benzyl bromide, respectively. The obtained yields were higher than 85% in all cases, unlike in the case of 5,5-dialkyl exo derivatives of type 3, which have been reported to give very poor yields of alkylation products, irrespective of the alkyl halides used.<sup>7</sup> Tricyclic adducts 4–11 underwent pyrolysis at temperatures of 250–290 °C for 2–6 days. Exo isomers needed longer reaction times to complete cycloreversion than endo isomers (Table I). Optical rotations of the obtained dialkylbutenolides 12–15, from endo and exo precursors, were in good accordance, verifying that configurational integrity of the starting butenolide 1 was respected through the overall sequence.

The configurational assignment of adducts 2 and 3 and alkylated adducts 4–11 was confirmed by a <sup>1</sup>H NMR study. Mainly, a trans disposition for protons H<sub>5</sub> and H<sub>6</sub> was confirmed by the value  $J_{5,6} = 4$  Hz.<sup>9</sup> In the case of benzylated lactones 10 and 11, the rather shielded absorption of the C-5 methyl groups (0.30 and 0.35 ppm, respectively) was attributed to the anisotropic effect of the nearby phenyl group. Furthermore, the two benzylic methylene protons showed chemical shifts differing in 1.18 (10) and 0.90 (11) ppm, thus indicating very different environments, as required by a predominant rotamer for both compounds. NOE experiments and molecular mechanics calculations (see supplementary material) supported that in both stereoisomers the major rotamer (82% population) had the phenyl group pointing to the methyl protons and one benzylic proton on top of the carbonyl bond.

The exploitation of the adducts in connection with the synthesis of chiral cyclopentane derivatives is under investigation.

### Experimental Section

Melting points were determined on a Kofler hot stage and are uncorrected. Optical rotations were obtained on a Propol polarimeter, Model Dr. Kernchen. Distillation of small amounts was effected on a rotational distillator, Büchi Model KRV 65/30

(only external or oven temperature given). The 70-eV electron-impact mass spectra were recorded with a Hewlett-Packard apparatus, Model 5985 B. IR spectra were recorded on a Perkin-Elmer spectrophotometer, Model 1310. The 80-MHz <sup>1</sup>H NMR and 20-MHz <sup>13</sup>C NMR spectra were recorded on a Bruker spectrometer Model WP 80 SY, from deuteriochloroform solutions; chemical shifts are given in parts per million relative to TMS ( $\delta$  scale). Microanalyses were performed at the Instituto de Química Bio-Orgánica, CSIC, Barcelona. Molecular mechanics calculations<sup>10</sup> were done on a VAX-11/780 system at Centre de Càlcul of the Universitat Autònoma de Barcelona.

**General Procedure for the Alkylation of Adducts 2 and 3.** To a solution of LDA (5 mmol) in anhydrous THF (40 mL) at -78 °C under an argon atmosphere was added a solution of adduct (2.5 mmol) in THF (4 mL), and the mixture was stirred for 1 h at -78 °C. Then, alkyl halide (10–20 mmol) was added. After 2 h at -78 °C, the solution was warmed to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with 1% aqueous HCl solution and with aqueous sodium thiosulfate, and dried over sodium sulfate. The solvents were removed, and the residue was chromatographed on silica gel (hexane-ether) to afford alkylated adducts 4–11.

(-)-(1*S*,2*R*,5*R*,6*S*,7*R*)-2,5-Dimethyl-4-oxatricyclo-[5.2.1.0<sup>2,6</sup>]dec-8-en-3-one (4): yield 100%; mp 77–79 °C; [α]<sub>D</sub><sup>20</sup> -51.2° (CHCl<sub>3</sub>, *c* 3.47); IR (CHCl<sub>3</sub>) 1740, 1560 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 179 (M + 1, 0.8), 113 (24.3), 83 (17.7), 66 (100.0); <sup>1</sup>H NMR 1.35 (3 H, CH<sub>3</sub>, d, *J* = 6.66 Hz), 1.51 (3 H, CH<sub>3</sub>, s), 1.63 (2 H, H<sub>10,10'</sub>, complex absorption), 2.23 (1 H, H<sub>6</sub>, dd, *J* = 4.00 Hz, *J'* = 2.66 Hz), 2.82 (1 H, H<sub>1</sub>, m), 3.05 (1 H, m), 4.00 (1 H, H<sub>5</sub>, dq, *J* = 6.66 Hz, *J'* = 2.66 Hz), 6.26 (2 H, H<sub>8</sub>, H<sub>9</sub>, complex absorption); <sup>13</sup>C NMR 180.22, 137.35, 134.14, 77.32, 55.07, 54.53, 51.69, 49.14, 46.27, 23.84, 23.49. Anal. Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.13; H, 7.92. Found: C, 73.79; H, 7.95.

(-)-(1*R*,2*R*,5*R*,6*S*,7*S*)-2,5-Dimethyl-4-oxatricyclo-[5.2.1.0<sup>2,6</sup>]dec-8-en-3-one (5): yield 92%; mp 107–109 °C; [α]<sub>D</sub><sup>20</sup> -59.6° (CHCl<sub>3</sub>, *c* 2.98); IR (CHCl<sub>3</sub>) 1735, 1555 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 179 (M + 1, 0.8), 113 (31.3), 66 (100.0); <sup>1</sup>H NMR 1.23 (3 H, CH<sub>3</sub>, s), 1.38 (3 H, CH<sub>3</sub>, d, *J* = 6.13 Hz), 1.55 (3 H, H<sub>6</sub>, H<sub>10,10'</sub>, complex absorption), 2.88 (2 H, H<sub>1</sub>, H<sub>7</sub>, m), 4.25 (1 H, H<sub>5</sub>, dd, *J* = 6.13 Hz, *J'* = 2.66 Hz), 6.25 (2 H, H<sub>8</sub>, H<sub>9</sub>, complex absorption); <sup>13</sup>C NMR 180.73, 137.18, 135.54, 79.16, 54.82, 54.13, 53.17, 50.04, 48.81, 44.99, 43.88, 23.44, 22.97, 21.96. Anal. Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.13; H, 7.92. Found: C, 73.86; H, 8.13.

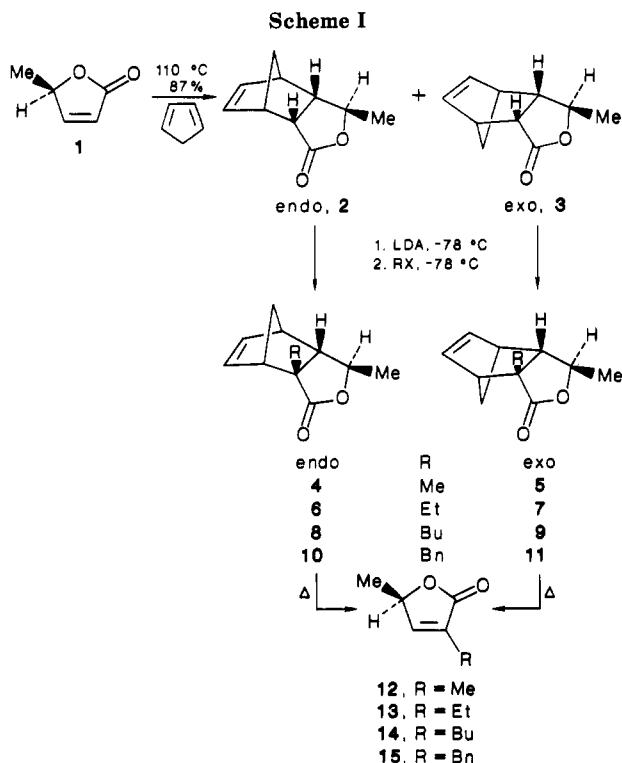
(-)-(1*S*,2*R*,5*R*,6*S*,7*R*)-2-Ethyl-5-methyl-4-oxatricyclo-[5.2.1.0<sup>2,6</sup>]dec-8-en-3-one (6): yield 87%; mp 84–86 °C; [α]<sub>D</sub><sup>20</sup> -50.3° (CHCl<sub>3</sub>, *c* 4.17); IR (CHCl<sub>3</sub>) 1755 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 193 (M + 1, 0.9), 127 (86.9), 85 (41.4), 83 (53.4), 66 (100.0), 65 (19.1), 47 (16.2); <sup>1</sup>H NMR 0.88–2.23 (4 H, complex absorption), 1.03 (3 H, t, *J* = 8.00 Hz), 1.36 (3 H, d, *J* = 6.13 Hz), 2.35 (1 H, dd, *J* = 4.53 Hz, *J'* = 3.20 Hz), 2.85 (1 H, m), 3.06 (1 H, m), 3.97 (1 H, dq, *J* = 6.66, *J'* = 3.20 Hz), 6.28 (2 H, complex absorption); <sup>13</sup>C NMR 179.67, 137.45, 135.13, 77.74, 60.78, 52.06, 51.41, 49.58, 46.34, 29.97, 22.19, 10.65. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>: C, 74.97; H, 8.39. Found: C, 75.22; H, 8.80.

(-)-(1*R*,2*R*,5*R*,6*S*,7*S*)-2-Ethyl-5-methyl-4-oxatricyclo-[5.2.1.0<sup>2,6</sup>]dec-8-en-3-one (7): yield 88%; mp 66–68 °C; [α]<sub>D</sub><sup>20</sup> -9.44° (CHCl<sub>3</sub>, *c* 4.02); IR (CHCl<sub>3</sub>) 1755, 1575 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 193 (M + 1, 4.1), 127 (89.7), 91 (25.1), 85 (22.8), 83 (36.1), 77 (15.6), 66 (100.0), 65 (32.3), 51 (15.1), 47 (16.3), 43 (37.5), 41 (29.9); <sup>1</sup>H NMR 0.78–2.10 (8 H, complex absorption), 1.38 (3 H, d, *J* = 6.66 Hz), 2.88 (1 H, m), 2.97 (1 H, m), 4.22 (1 H, dd, *J* = 6.66 Hz, *J'* = 2.66 Hz), 6.20 (2 H, complex absorption);

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<sup>13</sup>C NMR 180.20, 136.83, 136.20, 79.54, 60.52, 52.34, 49.86, 48.99, 44.88, 28.78, 22.16, 10.58. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>: C, 74.97; H, 8.39. Found: C, 74.98; H, 8.83.

(-)-(1*S*,2*R*,5*R*,6*S*,7*R*)-2-Butyl-5-methyl-4-oxatricyclo-[5.2.1.0<sup>2,6</sup>]dec-8-en-3-one (8): yield 83%; bp 120 °C (0.02 Torr); [α]<sub>D</sub><sup>20</sup> -50.9° (CHCl<sub>3</sub>, c 3.66); IR (neat) 1750, 1565 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 221 (M + 1, 0.9), 155 (89.7), 91 (18.7), 66 (100.0), 65 (23.5), 43 (26.7), 41 (27.2); <sup>1</sup>H NMR 0.72–2.18 (11 H, complex absorption), 1.35 (3 H, d, *J* = 6.66 Hz), 2.35 (1 H, dd, *J* = 4.00 Hz, *J'* = 2.66 Hz), 2.83 (1 H, m), 3.05 (1 H, m), 3.95 (1 H, dq, *J* = 6.66 Hz, *J'* = 2.66 Hz), 6.27 (2 H, complex absorption); <sup>13</sup>C NMR 179.64, 137.18, 135.04, 77.61, 59.86, 52.14, 51.54, 49.43, 46.26, 36.88, 28.38, 22.76, 22.09, 13.51. Anal. Calcd for C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>: C, 76.33; H, 9.15. Found: C, 76.66; H, 9.21.

(+)-(1*R*,2*R*,5*R*,6*S*,7*S*)-2-Butyl-5-methyl-4-oxatricyclo-[5.2.1.0<sup>2,6</sup>]dec-8-en-3-one (9): yield 86%; bp 120 °C (0.02 Torr); [α]<sub>D</sub><sup>20</sup> +4.5° (CHCl<sub>3</sub>, c 4.40); IR (neat) 1750, 1565 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 221 (M + 1, 0.9), 155 (100.0), 91 (21.1), 77 (19.1), 67 (18.7), 66 (97.1), 65 (25.8), 43 (31.3), 41 (26.8); <sup>1</sup>H NMR 0.70–1.97 (12 H, complex absorption), 1.40 (3 H, d, *J* = 6.66 Hz), 2.85 (1 H, m), 2.97 (1 H, m), 4.22 (1 H, dq, *J* = 6.66 Hz, *J'* = 2.66 Hz), 6.22 (2 H, complex absorption); <sup>13</sup>C NMR 180.38, 136.81, 136.28, 79.59, 59.77, 52.65, 50.09, 49.04, 44.80, 35.86, 28.49, 22.84, 22.22, 13.60. Anal. Calcd for C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>: C, 76.33; H, 9.15. Found: C, 76.54; H, 9.22.

(-)-(1*S*,2*R*,5*R*,6*S*,7*R*)-2-Benzyl-5-methyl-4-oxatricyclo-[5.2.1.0<sup>2,6</sup>]dec-8-en-3-one (10): yield 100% mp 122–124 °C; [α]<sub>D</sub><sup>20</sup> -6.8° (CHCl<sub>3</sub>, c 2.65); IR (CHCl<sub>3</sub>) 1750, 1605, 1580 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 254 (M, 0.8), 107 (58.5), 92 (100.0), 91 (51.0), 85 (45.8), 83 (72.2), 79 (85.7), 77 (74.6), 65 (35.2), 51 (33.0), 50 (18.3), 48 (18.0), 47 (33.5); <sup>1</sup>H NMR 0.32 (3 H, d, *J* = 6.66 Hz), 1.73 (2 H, complex absorption), 2.36 (1 H, dd, *J* = 4.00 Hz, *J'* = 2.66 Hz), 2.65 (1 H, d, *J* = 13.30 Hz), 3.00 (2 H, complex absorption), 3.58 (1 H, d, *J* = 13.30 Hz), 3.80 (1 H, dq, *J* = 6.66 Hz, *J'* = 2.66 Hz), 6.30 (2 H, complex absorption), 6.97–7.53 (5 H, complex absorption); <sup>13</sup>C NMR 179.80, 137.55, 137.03, 135.71, 129.92, 128.53, 126.90, 78.17, 62.50, 52.16, 50.48, 49.69, 46.58, 42.84, 20.66. Anal. Calcd for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>: C, 80.28; H, 7.13. Found: C, 80.53; H, 7.50.

(+)-(1*R*,2*R*,5*R*,6*S*,7*S*)-2-Benzyl-5-methyl-4-oxatricyclo-[5.2.1.0<sup>2,6</sup>]dec-8-en-3-one (11): yield 96%; mp 88–90 °C; [α]<sub>D</sub><sup>20</sup> +61.6° (CHCl<sub>3</sub>, c 1.92); IR (CHCl<sub>3</sub>) 1750, 1605, 1580 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 254 (M, 3.6), 189 (100.0), 143 (58.7), 129 (17.9), 128 (27.6), 115 (39.8), 91 (77.5), 85 (69.2), 83 (94.0), 77 (19.4), 66 (94.5), 65 (34.9), 51 (19.0), 48 (26.5), 47 (48.3); <sup>1</sup>H NMR 0.37 (3 H, d, *J* = 6.66 Hz), 1.41–1.80 (3 H, complex absorption), 2.22

(1 H, d, *J* = 13.33 Hz), 2.85 (1 H, br s), 3.07 (1 H, m), 3.40 (1 H, d, *J* = 13.33 Hz), 4.03 (1 H, dq, *J* = 6.66 Hz, *J'* = 2.66 Hz), 6.35 (2 H, complex absorption), 6.90–7.45 (5 H, complex absorption); <sup>13</sup>C NMR 180.22, 138.03, 137.30, 136.50, 129.78, 128.30, 126.66, 79.98, 62.77, 50.66, 50.04, 49.03, 44.92, 41.28, 20.31. Anal. Calcd for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>: C, 80.28; H, 7.13. Found: C, 80.15; H, 7.06.

**General Procedure for the Pyrolysis of Adducts 4–11.** Specific conditions of temperature, time, and solvent used in each case are listed in Table I, as well as yields and optical rotations of the resulting butenolides. A typical experiment was run as follows: A solution of the adduct (2 mmol) in a solvent (60 mL) was heated in a sealed tube. The solvent was distilled and the residue chromatographed on silica gel (hexane–ether) to afford the butenolides.

(-)-(R)-3,5-Dimethyl-2(5H)-furanone (12): bp 120 °C (16 Torr) [lit.<sup>11</sup> bp 100–103 °C (45 Torr)]; IR (neat) 1750, 1665 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.40 (3 H, d, *J* = 7.21 Hz), 1.92 (3 H, t, *J* = 1.60 Hz), 4.98 (1 H, q, *J* = 7.21 Hz), 7.01 (1 H, q, *J* = 1.60 Hz); <sup>13</sup>C NMR 173.89, 149.84, 128.92, 77.01, 18.55, 9.94.

(-)-(R)-3-Ethyl-5-methyl-2(5H)-furanone (13): bp 130 °C (13 Torr) [lit.<sup>5</sup> bp 59–62 °C (0.57 Torr)]; IR (neat) 1750, 1650 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.16 (3 H, t, *J* = 7.20 Hz), 1.40 (3 H, d, *J* = 7.21 Hz), 2.30 (2 H, q, *J* = 7.20 Hz), 5.0 (1 H, q, *J* = 7.21 Hz), 7.01 (1 H, m); <sup>13</sup>C NMR 173.36, 148.33, 135.16, 77.17, 18.77, 18.24, 11.41.

(-)-(R)-3-Butyl-5-methyl-2(5H)-furanone (14): bp 90 °C (0.1 Torr) [lit.<sup>12</sup> [α]<sub>D</sub><sup>20</sup> +11.7° (CHCl<sub>3</sub>, c 0.16) for the (+)-*S* enantiomer; no bp given]; IR (neat) 1750, 1650 cm<sup>-1</sup>; <sup>1</sup>H NMR 0.92 (3 H, m), 1.05–1.73 (4 H, complex absorption), 2.23 (2 H, complex absorption), 1.39 (3 H, d, *J* = 7.21 Hz), 4.96 (1 H, q, *J* = 7.21 Hz), 6.96 (1 H, m); <sup>13</sup>C NMR 173.63, 148.90, 133.93, 77.19, 29.33, 24.63, 22.02, 18.94, 13.46.

(-)-(R)-3-Benzyl-5-methyl-2(5H)-furanone (15): bp 120 °C (0.02 Torr); IR (neat) 1750, 1600, 1655 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.37 (3 H, d, *J* = 7.21 Hz), 3.57 (2 H, m), 4.97 (1 H, q, *J* = 7.21 Hz), 6.82 (1 H, m), 7.22 (5 H, complex absorption); <sup>13</sup>C NMR 173.02, 150.30, 137.24, 133.43, 128.56, 128.39, 126.42, 77.35, 31.33, 18.31. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>: C, 76.57; H, 6.43. Found: C, 76.61; H, 6.68.

**Acknowledgment.** Financial support from “Comisión Asesora de Investigación Científica y Técnica” (projects 2013/83 and PB85-0244) is gratefully acknowledged. We thank Dr. C. Jaime for helpful advising in molecular mechanics calculations.

**Registry No.** 2, 111533-91-6; 3, 111613-19-5; 4, 115093-25-9; 5, 115181-93-6; 6, 115183-48-7; 7, 115093-26-0; 8, 115183-49-8; 9, 115093-27-1; 10, 115093-28-2; 11, 115181-94-7; 12, 59417-65-1; 13, 115093-29-3; 14, 115093-30-6; 15, 115093-31-7; ethyl bromide, 74-96-4; butyl bromide, 109-65-9; benzyl bromide, 100-39-0.

**Supplementary Material Available:** Data from NOE experiments and from molecular mechanics calculations (2 pages). Ordering information is given on any current masthead page.

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### A Stereodivergent Synthesis of D-erythro-Sphingosine and D-threo-Sphingosine from L-Serine

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Received March 8, 1988

The sphingosine bases are a group of long-chain amino alcohols incorporated into the structures of various glycosphingolipids.<sup>1</sup> These compounds are important mem-