a solution of 2-bromophenol (6.67 mL, 0.058 mol) in DME (20 mL). After evolution of H_2 had ceased, the mixture was cooled to −30 °C, and a solution of 3,5-dibromocyclopentene[4] (6.24 g, 0.0267 mol) in DME (25 mL) was added. The mixture was warmed to rt and was stirred for 1 day. After evaporation of the solvent, the residue was dissolved in EtOAc (300 mL). The solution was washed with brine (20 mL × 2) and 1 N aqueous NaOH (20 mL). The solution was then dried (Na_2SO_4). Activated carbon (15 g) was added, and the mixture was warmed at 60 °C. The mixture was filtered. Concentration of the filtrate gave **12** (6.0 g, 0.015 mmol, 53%) as an almost pure white solid: mp 138–139 °C; ^{1}H NMR (100 MHz) δ 2.21 (dt, J = 5.0, 14.0 Hz, 1 H), 3.08 (q, J = 7.0, 14.0 Hz, 1 H), 5.20 (dd, J = 5.0, 7.0 Hz, 2 H), 6.30 (s, 2 H), 6.8–7.6 (m, 8 H); IR (KBr) 1585, 1473, 1440, 1272, 1165, 1130, 1050, 992, 790, 760, 750 cm^{-1}; MS m/e 239 (M^+ − 171, 171 = C_6H_4BrO), 237, 175, 172, 171, 158. Anal. Calcd for $C_{17}H_{14}Br_2O_2$: C, 49.66; H, 3.68. Found C, 49.66; H, 3.56.

Synthesis of 3a,8b-*cis*-Dihydro-3*H*-cyclopenta[*b*]benzofuran (14). To a stirred solution of 3,5-*cis*-bis(2-bromophenoxy)-2-cyclopentene (**12**) (6.0 g, 14.6 mmol) in THF (80 mL) at −50 °C was slowly added *n*-BuLi (2.0 N solution in hexane, 11 mL, 22 mmol). After 1 h, the solution was warmed to −10 °C and stirred for 3 h. Then brine (5 mL) was added. The mixture was concentrated. The residue was dissolved in Et_2O (300 mL). The solution washed with 1 N aqueous NaOH (20 mL) and brine (30 mL) and then was dried (Na_2SO_4) and concentrated. The residual oil was purified by column chromatography on silica gel (cyclohexane/EtOAc, 95:5) to give **14** as colorless oil (1.84 g, 11.7 mmol, 80%): ^{1}H NMR (100 MHz) δ 2.80 (dd, J = 0.5, 2.2 Hz, 1 H), 2.82 (dd, J = 0.5, 5.2 Hz, 1 H), 4.35 (d, J = 7.8 Hz, 1 H), 5.43 (m, 1 H), 5.71 (s, 2 H, olefinic), 6.7–7.6 (m, 4 H); ^{13}C (67.9 MHz) 40.58, 54.22, 86.33, 109.33, 120.19, 124.16, 128.02, 128.74, 128.94, 131.10, 159.49; IR (film) 1602, 1590, 1472, 1457, 1220, 1160, 1095, 900, 860, 827, 790, 750, 700 cm^{-1}; MS m/e 158 (M^+), 131, 115.

Preparation of 3,5-*cis*-Bis(2,6-dibromophenoxy)-2-cyclopentene (15). To a suspension of NaH (5.6 g, 0.117 mol) and DME (100 mL) at 0 °C was slowly added a solution of 2,6-dibromophenol[8] (29.4 g, 0.117 mol) in DME (159 mL). After the evolution of H_2 had ceased, 18-crown-6 (280 mg) and 3,5-dibromocyclopentene[5] (12.0 g, 0.053 mol) were added. The mixture warmed to rt and was stirred for 3 days. The white precipitate that formed was collected by filtration and were warmed (ca. 3 × 20 mL). Then it was dissolved in $CHCl_3$. The solution was dried ($MgSO_4$). Concentration gave almost pure **15** (22.6 g, 0.040 mol, 75%): mp 105–206 °C; ^{1}H NMR (100 MHz) δ 2.90 (dt, J = 8.0, 8.0, 16.0 Hz, 1 H), 3.12 (dt, J = 7.0, 7.0, 8.0 Hz, 1 H), 5.10 (dd, J = 7.0, 8.0 Hz, 1 H), 6.31 (s, 2 H, olefinic), 6.83 (t, J = 8.0 Hz, 1 H), 7.52 (d, J = 8.0, 8.0 Hz, 2 H); IR (KBr) 1550, 1430, 1375, 1235, 1068, 1015, 988, 960, 935, 895, 820, 760, 740, 715 cm^{-1}; MS m/e 572, 571, 570, 569, 568, 567, 566, 565, 564(M^+), 319, 317, 315. Anal. Calcd for $C_{17}H_{12}Br_4O_2$: C, 35.95; H, 2.13. Found: C, 35.86; H, 2.19.

Preparation of 3a,8b-*cis*-Dihydro-3*H*-5-bromocyclopenta[*b*]benzofuran (16). To a suspension of the tetrabromide **15** (87.1 g, 1.153 mol) in THF (300 mL) at 40 °C was added cyclohexylmagnesium bromide (140 mL of 2.18 M solution in THF). The mixture was stirred for 20 min, and then CuI (0.58 g) was added at room temperature. The mixture was stirred for 30 min and then was filtered. The filtrate was concentrated. The residue was dissolved in cyclohexane. The solution was washed with 5% aqueous NaOH, dried, and concentrated to give ca. 60 g of an oily material. This was distilled under reduced pressure (60–62 °C/10^{-3}) to afford 26.0 g (0.11 mol, 72%) of pure crystals of **16**: mp 38–39 °C; ^{1}H NMR (100 MHz) δ 2.90 (m, 2 H), 4.80 (d, J = 8.0 Hz, 1 H), 5.54 (dt, J = 4.0, 4.0, 8.0 Hz, 1 H), 5.66 (m, 2 H), 6.70 (t, J = 8.0, 8.0 Hz, 1 H), 7.20 (m, 2 H); ^{13}C (67.9 MHz) 40.61, 55.12, 87.05, 102.45, 121.69, 123.18, 129.57, 130.29, 130.55, 131.16, 156.84; IR (film) 3060, 2950, 1600, 1585, 1480, 1220, 1162, 1130, 1050, 945, 860, 832, 770, 750, 740, 710 cm^{-1}; MS m/e 238, 236 (M^+), 209, 211, 128. Anal. Calcd for $C_{11}H_9OBr$: C, 55.72; H, 3.83; Br, 33.80. Found: C, 55.46; H, 3.82; Br, 34.10.

Preparation of 3,5-*cis*-Bis(2,4,6-tribromophenoxy)cyclopentene (17). In a manner similar to that used to prepare **15**, **17** (131 g, 0.133 mol, 51%) was prepared from 2,4,6-tribromophenol (193 g, 0.509 mol) and 3,5-dibromocyclopentene (59 g, 0.26 mol). **17**: mp 253–254 °C; ^{1}H NMR (100 MHz) δ 2.73 (m, 1 H), 3.06 (m, 1 H), 5.05 (m, 2 H), 6.24 (s, 2 H), 7.68 (s, 4 H); IR (KBr) 1600, 1570, 1470, 805, 780 cm^{-1}; MS m/e 393 (M^+ − 327), 327.

Preparation of 3a,8b-*cis*-Dihydro-3*H*-5,7-dibromocyclopenta[*b*]benzofuran (18). To a stirred suspension of the hexabromide **17** (50 g, 0.069 mol) in THF (172 mL) at 40 °C was added cyclohexylmagnesium bromide (32 mL of a 2.1 M solution in THF). After 30 min of stirring, CuI (0.58 g) was added at rt. The mixture was stirred for 30 min and then was filtered. The residue was purified by column chromatography on silica gel (cyclohexane) to afford 20 g of crude product. Recrystallization (EtOAc/cyclohexane) gave **18** (15 g, 0.0457 mol, 69%): mp 110–112 °C; ^{1}H NMR (100 MHz) δ 2.90 (m, 2 H), 4.48 (m, 1 H), 5.60 (m, 1 H), 5.80 (m, 2 H), 7.25 (d, J = 2.0 Hz, 1 H), 7.40 (d, J = 2.0 Hz, 1 H); ^{13}C NMR (67.9 MHz) 40.59, 55.06, 87.74, 103.06, 112.10, 126.32, 130.00, 130.12, 132.02, 133.20, 156.38; IR (KBr) 3070, 2980, 2920, 1585, 1570, 865, 830, 740, 718 cm^{-1}. Anal. Calcd for $C_{11}H_8OBr_2$: C, 41.81; H, 2.55; Br, 50.58. Found: C, 41.67; H, 2.53; Br, 50.60.

Registry No. **1**, 578-57-4; **2**, 104-92-7; **3**, 21702-84-1; **4**, 38603-09-7; **5**, 607-99-8; **6**, 5424-43-1; **7**, 25245-34-5; **8**, 74076-59-8; **9**, 2674-34-2; **11**, 17040-70-9; **12**, 84598-97-0; **14**, 66324-29-6; **15**, 79020-64-7; **16**, 84599-03-1; **17**, 84491-98-5; **18**, 84599-02-0; *i*-PrMgO, 1068-55-9; MeMgBr, 75-16-1; *i*-PrMgBr, 920-39-8; c-$C_6H_{11}MgCl$, 931-51-1; anisole, 100-66-3; 2-allyl-4-bromoanisole, 114303-65-0; 5-bromo-2-methoxybenzoic acid, 2476-35-9; 4-bromo-2-iodoanisole, 98273-59-7; 4-bromo-2-(1-hydroxy-*n*-butyl)anisole, 137464-94-9; allyl bromide, 106-95-6; 2-bromophenol, 95-56-7; 2,6-dibromophenyl, 608-33-3; 2,4,6-tribromophenol, 118-79-6.

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The Absolute Configuration of (*R*)-(−)-(4-Methylcyclohexylidene)acetic Acid[1]

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A recent paper by Salvadori et al.[3] concerning the lack of correspondence between the experimental and theoretical values for the circular dichroism (cd) spectra of the long wavelength $\pi-\pi^*$ for a number of chiral 1,3-dienes[4] prompts this report. Calculations using De Voe coupled oscillator theory or a semiempirical MO-SCF method (CND/S) yielded cd signs opposite to those found experimentally[4] for a series of s-trans chiral planar (cyclohexylidene)propenes **1**. The same result is obtained in using Weigang's amplified sector rule.[5] Although the absolute configurations of **1** had been confidently established by chemical correlations,[4a,6] because of Salvadori's findings it was thought desirable to confirm the absolute configurations of one of the key intermediates, Gerlach's

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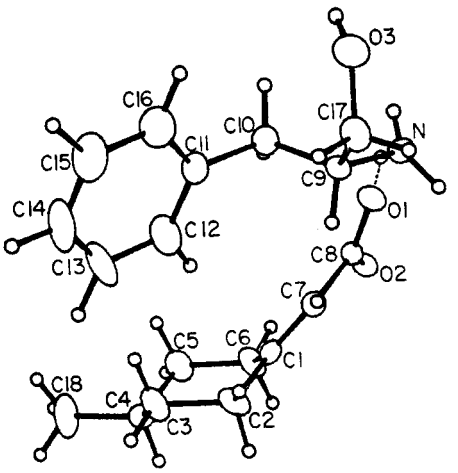
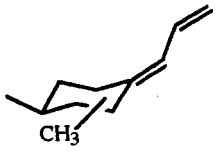
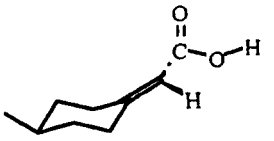


Figure 1. ORTEP plot of (*R*,*R*)-(−)-**3**.

acid,[7] which was reported[7] to have the (*R*)-(−)-**2** configuration.

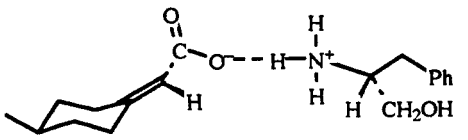


1



(R)-(−)-**2**

Initially, it was our desire to react (−)-**2** with (*R*)-(+)-3-phenyl-2-aminopropanol (phenylalaninol) to form the diastereomeric amide which could then be subjected to X-ray analysis. The use of trimethylsilyl chloride/triethylamine procedure was selected to carry out this transformation. In our hands no amide was formed[8] but instead a 92% yield of the salt **3** was obtained, mp 138–140 °C, $[\alpha]^{25}_{Hg}$ −42° (*c* 0.1, EtOH). The X-ray structure is shown in Figure 1 and clearly confirms the assignment by Gerlach for the absolute configuration of **2** as (*R*)-(−).



(R,R)-(−)-**3**

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(8) We suspect that this was due to the rapid hydrolysis of the trimethylsilylate by the wet phenylalaninol.

Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. Infrared spectra were measured with Perkin-Elmer Model 257 grating spectrophotometer. The 1601 cm^{-1} absorption band of polystyrene film was used to calibrate the chart paper. Optical rotations were measured on a Bendix-Ericson Model 987 ETL/NPL polarimeter equipped with a Bendix Model DR-1 digital display.

(*R*,*R*)-(−)-3. To a solution of 0.30 g (2 mmol) of (*R*)-(−)-(4-methylcyclohexylidene)acetic acid ($[\alpha]^{25}_{Hg}$ −86°, EtOH, 90% optically pure) dissolved in 5 mL of benzene was added 0.28 mL (2 mmol) of triethylamine followed by 0.26 mL (2 mmol) of trimethylsilyl chloride. After the mixture was stirred for 15 min at ambient temperature the precipitate of triethylamine hydrochloride was filtered and washed with pentane. The combined filtrates were concentrated in vacuo to 5 mL, and 0.6 g of (*R*)-(+)-3-phenyl-2-aminopropanol (phenylalaninol, Aldrich) was added. The mixture was allowed to stir overnight and the crystalline product filtered to yield 563 mg (92%) of product, mp 134–7 °C. Recrystallization from acetone–hexane gave: mp 138–40 °C; $[\alpha]^{25}_{Hg}$ −42° (*c* 0.1, EtOH); IR (mull) 2800–2300 (br), 2170, 1635 cm^{-1}.

X-ray Analysis of (*R*,*R*)-(−)-3. Single crystals of $C_{18}H_{27}O_3N$ were grown by slow evaporation the ethyl acetate–hexane solution of the compound. The crystals were orthorhombic, space group $P2_12_12_1$ with a = 4.996 (1) Å, b = 11.052 (2) Å, c = 32.683 (4) Å, and $d_{calc'd}$ = 1.124 g cm^{-3} for Z = 2 ($M\gamma$ = 305.42). The intensity data were measured on a CAD4 Enraf Nonius diffractometer (Mo radiation, monochromated, w scans). The size of the crystal used for collection was approximately 0.2 × 0.2 × 0.3 mm^3. No absorption correction was necessary (μ = 0.706). A total of 1885 reflections were measured for 20 ≤ 50°, of which 1244 were considered to be observed [$I \geq 2\sigma(I)$]. The structure was solved by direct methods using MULTAN 78[9] and refined by full-matrix least-squares.[10] In the final refinement anisotropic thermal parameters were used for non-hydrogen atoms. Methyl, amine, and hydroxyl hydrogen atoms were located from a difference Fourier map; the remaining hydrogen and hydroxyl hydrogen atom parameters were calculated assuming idealized geometry. Hydrogen atom contributions were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices were R = 0.055 and R_w = 0.06 for the 1244 observed reflections. The final difference Fourier map was essentially featureless with no peaks greater than 0.3 e $Å^{-3}$.

Registry No. (*R*)-(−)-**2**, 28835-95-2; (*R*,*R*)-(−)-**3**, 137571-67-6.

Supplementary Material Available: Tables 1–4 listing summary of crystal data, bond angles, bond lengths, and positional and thermal parameters including their estimated standard deviations (5 pages). Ordering information is given on any current masthead page.

(9) Main, P. *MULTAN 78. A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; Department of Physics, University of York, York, England.
(10) All computations were performed on a PDP 11/34 computer with the aid of the Structure Determination crystallographic program library obtained with the purchase of the X-ray equipment.