(57), 121 (65); ^{1}H NMR δ 0.9-1.1 (m, 12 H containing s at 1.08), 1.2-2.1 (m, 12 H).

α-Bromination of 85 mg (0.39 mmol) of **58** and the subsequent dehydrobromination as described above gave 73 mg (86% yield) of (±)-**5** after flash chromatography (10% ether) whose spectral data (IR, ^{1}H and ^{13}C NMR) were identical with those of the natural product.[5]

(1*R,5*R**,8*R**,9*S**)-5,9-Dimethyltricyclo[6.3.0.0^{1,5}]undec-3-en-2-one (50).** To a solution of 189 mg (1.00 mmol) of **49** in 1.8 mL of methyl alcohol (MeOH) was added 0.7 mL (6.90 mmol) of 30% hydrogen peroxide (H_2O_2) at 0 °C. The solution was stirred at 0 °C for 10 min and 0.35 mL (2.10 mmol) of 25% sodium hydroxide (NaOH) solution was added. The solution was stirred at 0 °C for 30 min and ice-water was added. The product was isolated by ether extraction (B), and flash chromatography (10% ether) of the crude material gave 6 mg of recovered **49** and 180 mg (91% yield) of the epoxy ketone **59** as a single product: IR 1730, 1370, 850 cm^{-1}; MS *m/e* 206 (M$^+$, 18), 149 (100); ^{1}H NMR δ 1.01 (d, *J* = 5.1 Hz, 3 H), 1.03 (s, 3 H), 1.2-2.2 (m, 10 H), 3.42 (d, *J* = 2.3 Hz, 1 H), 3.66 (d, *J* = 2.3 Hz, 1 H). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.95; H, 8.96.

To a solution of 119 mg (0.58 mmol) of **59** in 0.5 mL of MeOH was added 0.10 mL (1.82 mmol) of 80% $N_2H_4 \cdot H_2O$ via a syringe at 0 °C under a nitrogen atmosphere. The solution was stirred at 0 °C for 5 min and 7.14 μL (0.13 mmol) of acetic acid was added dropwise via a syringe.[24] The solution was stirred at 0 °C for 10 min and then at room temperature for 4 h and brine was added. The product was isolated by ether extraction (B), and flash chromatography of the crude material gave 79 mg (10% ether eluent) of recovered **59** of 21 mg (57% yield, elution with 15% ether) of the allyl alcohol **60**: IR 3500-3050, 3020, 1600, 1010, 940, 780 cm^{-1}; MS *m/e* 192 (M$^+$, 100), 177 (52), 150 (49), 148 (40), 135 (39), 109 (53), 108 (51), 107 (51), 97 (89), 81 (48); ^{1}H NMR δ 0.8-2.2 (m, 17 H containing d at 0.97, *J* = 4.9 Hz, and s at 1.02), 4.23 (bd s, 1 H), 5.73 (d, *J* = 5.7 Hz, 1 H), 5.85 (dd, *J* = 5.7, 2.3 Hz, 1 H).

A mixture of 37 mg (0.19 mmol) of **60** and 112 mg (0.29 mmol) of pyridinium dichromate[25] in 2 mL of CH_2Cl_2 was stirred at room temperature for 3 h. Flash chromatography (10% ether) of the mixture gave 33 mg (97% yield) of **50**, whose spectral data (IR, ^{1}H and ^{13}C NMR) were identical with those of (+)-**50**, provided by Prof. Paquette.[6a]

Acknowledgment. We thank Professor M. Fetizon and Dr. J. Boivin of Ecole Polytechnique for valuable suggestions about the rearrangement pathways and Professors F. Bohlmann of Technical University Berlin and L. A. Paquette of The Ohio State University for generous supplies of copies of the original IR and ^{1}H NMR spectra of (−)-**5** and (+)-**50**, respectively.

Supplementary Material Available: Details of preparation of cyclobutyl ketones **8-22** and structure determination of the starting and rearranged ketones, Experimental Section except for that described in the text, Tables II-VII listing final atomic parameters, final anisotropic thermal parameters, bond length, and bond angles of **7**, and a figure of **7** (45 pages). Ordering information is given on any current masthead page.

Nucleophile-Selective Iodocyclizations: Butyrolactone versus Tetrahydrofuran Formation

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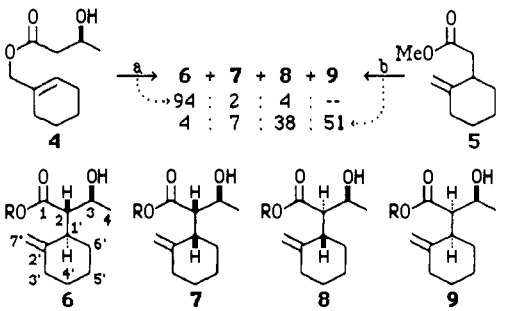
Abstract: Nucleophile selectivity in the electrophilic cyclization of substrates like **3** has been investigated in the context of efficient chemo- and stereoselective functionalization of 3-hydroxy-2-(2-methylenecyclohexan-1-yl)butyric acids (cf., **6-9**) via iodocyclization. In addition, composite nucleophile selectivities for this diastereomeric series were used to probe the reliability of ground-state conformational analysis as an indicator of relative reactivities for the various conformations of **3**. The results provide unambiguous evidence for $C_{1'}$,C_2,C_3 stereocontrol in these kinetic iodocyclizations.

The electrophilic cyclization reaction[2] is a multipurpose transformation, which continues to receive methodological[3] and synthetic[4] attention, particularly in regard to the stereocontrolled elaboration of highly functionalized heterocycles. We recently reported[5] the efficient and highly stereoselective functionalization of heptadienoate **1** via its iodolactonization (Figure 1). Indeed, of the four possible iodolactonization products of **1**, **2** was formed almost exclusively, the result of 147:1 group (i.e., olefin) and 30:1 face selectivities. It was noted that this impressive kinetic preference, the consequence of a transition-state bias capable of differentiating the two diastereotopic olefins, is mirrored in the

Scheme I



[a](i) 2 equiv of LDA, THF, −78 °C. (ii) −78 °C → 50 °C. (iii) H_3O^+. (iv) CH_2N_2, ether. [b](i) LDA, THF, −78 °C. (ii) CH_3CHO. (iii) H_3O^+.

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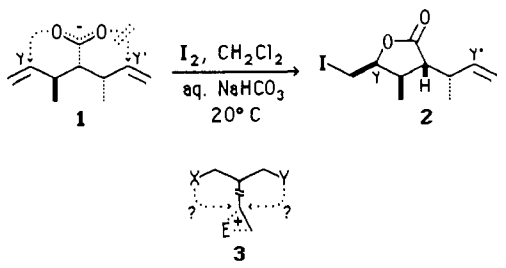

Figure 1.

ground-state conformational bias of **1**. In parallel to that process, one can envision construction of an acyclic substrate such as **3** in which two different nucleophiles (X and Y) compete for a single electrophilic center. On the basis of our results with **1**, we postulated that manipulation of the conformation of **3** through a diastereomeric series of substrates (cf., **6–9**) could allow for controlled delivery of either nucleophile to the electrophilic center resulting in X- or Y-heterocycle formation. Composite nucleophile selectivities for this series would uniquely probe the reliability of ground-state conformational analysis as an indicator of relative reactivities for the various conformations of **3**.[6] Herein, we report the details of that study in the context of efficient chemo- and stereoselective functionalization of 3-hydroxy-2-(2-methylenecyclohexan-1-yl)butyric acids (analogues of **3**, cf. **6**) via iodocylization, *transformations that proceed with concomitant group and face selectivity*.

In our ongoing study of the dianionic Claisen rearrangement of allyl 3-hydroxybutanoates,[7] it became apparent to us that the products of these [3,3]-sigmatropic rearrangements (cf. **4** → **6–9**) were suitably arrayed for this iodocyclization study. That the X and Y groups of **3** are both oxygens whose conjugate acids would be of comparable acidity, and hence of comparable nucleophilicity,[8] and that the carboxy nucleophilicity can be varied (i.e., $-COO^-$ vs $COOCH_3$)[9] were considered important advantages for these substrates in the current investigation. Thus, methylenecyclohexaneacetic acid derivatives **6–9** were prepared and subjected to kinetic iodocyclization[2c] conditions; as was hoped, the composite nucleophile selectivities were predicted by a ground-state conformational analysis for each substrate and provide unambiguous evidence for $C_{1'},C_2,C_3$ stereocontrol in the ensuing kinetic iodocyclization reaction.

Methylenecyclohexaneacetic acid derivatives **6–9** were synthesized as outlined in Scheme I. Thus, 3-hydroxybutanoate **4** was subjected to our dianionic Claisen protocol and the crude reaction mixture esterified with diazomethane producing esters **6–8** in a 94:2:4 ratio, respectively (50% combined yield). Medium-pressure liquid chromatography (MPLC) of this mixture gave **6** contaminated by only trace amounts of ester **7**. In contrast, condensation of the lithium enolate of ester **5** with acetaldehyde produced methylenecyclohexaneacetates **6–9** in a 4:7:38:51 ratio, respectively (77% combined yield). This time, MPLC furnished diastereomers **8** and **9**, both in pure form. Ester **7**, a minor constituent in each preparation,[10] coelutes with **6** on MPLC purification and thus was not available in pure form.

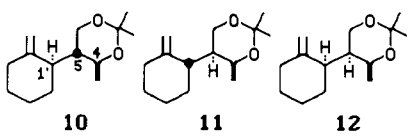

Figure 2.

NMR-based $C_{1'},C_2,C_3$ stereochemical assignments for esters **6–9** proved inconclusive. In fact, unambiguous assignment of the C_2,C_3 stereochemistry required reduction of the carboxy group ($LiAlH_4$, ether) and subsequent dioxane formation (2,2-dimethoxypropane, Amberlyst-15) to provide a rigid framework with interpretable ^1H NMR coupling constants. In analogy with earlier results from these laboratories,[7] H_4,H_5 coupling constants for the resulting dioxolanes (Figure 2: **10**, an axial–axial $J_{4,5}$ of 8.9 Hz; **11**, an axial–equatorial $J_{4,5}$ of 3.58 Hz; **12**, an axial–equatorial $J_{4,5}$ of 3.47 Hz) unequivocally define the C_2,C_3 stereochemistry of esters **6–9**.

$H_{1'},H_2$ coupling constants in the methylenecyclohexaneacetates **6–9** ($J_{1',2}$ = 11–11.4 Hz) were entirely undiagnostic of $C_{1'},C_2$ stereochemistry and suggested that the H_1–C–C–H_2 dihedral angle in each compound is nearly 180°. In dioxolanes **10–12**, unresolved resonances preclude determination of $H_{1'},H_5$ coupling constants. Thus, while a tentative assignment of $C_{1'},C_2,C_3$ relative stereochemistry for **6** could be made on the basis of our previous dianionic Claisen studies, we turned to an investigation of the kinetic iodocyclization of methylenecyclohexaneacetates **6–9** (Scheme II) with the question of $C_{1'},C_2$ stereochemistry left temporarily unresolved.

In our first cyclization experiment, carboxylic acid **6** (R = H) underwent electrophilic cyclization (I_2, aqueous $NaHCO_3$, CH_2Cl_2, 20 °C)[11] to give exclusive formation of iodolactone **13** (87% yield); no trace of iodotetrahydrofuran **14**, the product of hydroxyl participation in the cyclization, was detected in the crude reaction mixture. Treatment of the corresponding methyl ester (**6**; R = CH_3) with iodine under identical conditions also gave only lactone formation (79% yield) in spite of the attenuated reactivity of the carbomethoxy substituent relative to the carboxy substituent. Our second substrate, methyl ester **9** (R = CH_3), was exposed to iodine (aqueous $NaHCO_3$, CH_2Cl_2, 20 °C) and, in contrast to **6**, it gave iodotetrahydrofuran **20** (88% yield) by hydroxyl cyclization to the complete exclusion of iodolactone **19**, the would-be product of carbomethoxy cyclization. Perhaps more significantly, carboxylic acid **9** (R = H) also undergoes cyclization only via the hydroxyl group, again producing iodotetrahydrofuran **20** (66% yield) and none of iodolactone **19**.

In considering these results, we became intrigued with the possibility of using minimum energy conformations for methylenecyclohexaneacetates **6–9** as a qualitative indicator of product selectivity in the ensuing iodocyclization. Thus, for each of these substrates, conformations with the butanoate side chain in both axial and equatorial positions were studied using Allinger's MM2 program.[12] Minimizations were then done for 120° rotations about the $C_{1'}$–C_2 and C_2–C_3 bonds and those lowest energy conformations leading to cis-fused iodolactones (**13**, **15**, **17**, **19**) or cis-fused iodotetrahydrofurans (**14**, **16**, **18**, **20**) are depicted in Scheme II (relative conformational energies shown parenthetically).[13] For example, consider the conformations available to **6**; only **6a** where the carboxy group is in proximity to the C=C and **6b** where the hydroxyl group is in proximity to the C=C are pertinent. The remarkable nucleophile selectivity manifested by **6** matches that anticipated on the basis of these ground-state

(6) Note: while the exceptional stereoselectivity observed in the cyclization of *d,l*-**1** is a manifestation of this predictive tool, a series consisting of *d,l*-**1** and its two meso diastereomers does not provide a general probe of this ground-state conformation/relative reactivity correlation since, in two of the three diastereomers, the two olefins are enantiotopic. Consequently, this diastereomeric series cannot accommodate the conformational maneuvers required to probe this correlation.

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(9) (a) The pK_a of a protonated ester is about −6.5[9b] while that of a carboxylic acid is about 4.7. On the basis of Bordwell consideration, the carboxylate is expected to be a much better nucleophile than the ester. (b) Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 324.

(10) (a) Attempted preparation of **7** from **9** by Mitsunobu hydroxyl inversion[10b] was thwarted by elimination to the α,β-unsaturated ester. (b) Swain, M. L.; Turner, R. W. *J. Chem. Soc., Chem. Commun.* **1981**, 840.

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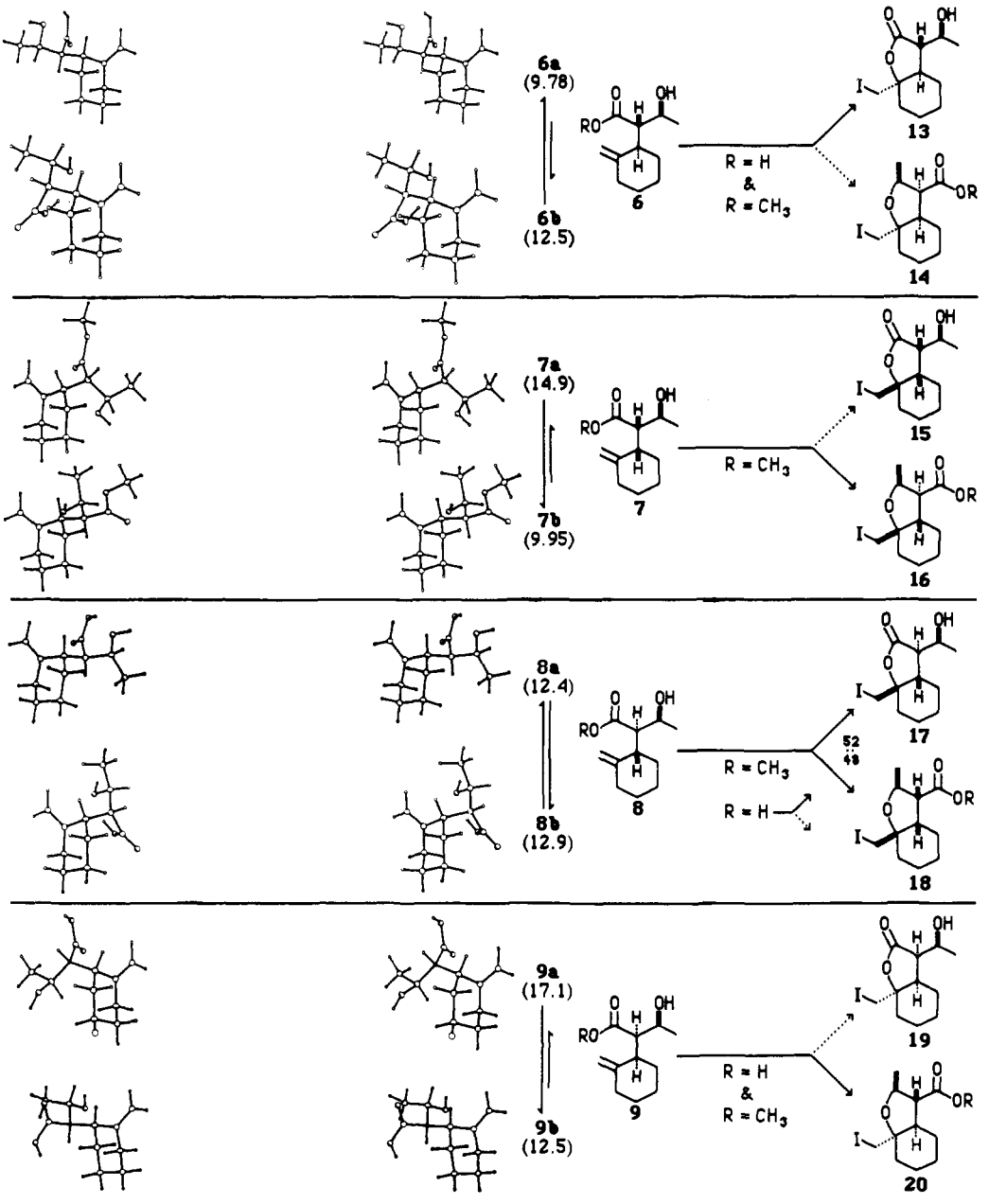
(12) MM2 1977 Allinger-QCEP395 and MMP1 Pi Allinger-PCEP318, which includes model parameters by Still and atom and trial constants by K. E. Gilbert and J. J. Gajewski, Indiana University.

(13) For each structure **6–9**, there is one conformation with an equatorial butanoate suitably orientated for cis iodocyclization. However, it is interesting to note that these four equatorial conformations are significantly higher in energy than the axial conformations depicted in Scheme II.

Scheme II. MM2 Calculations[a] for Methylenecyclohexaneacetates **6**,[b] **7**,[c] **8**[b] and **9**[c]



[a] MM2 conformational energies are given parenthetically in kcal/mol. [b] *For* **6** and **8**, MM2 minimizations were done with the carboxylic acid proton H-bonded to the hydroxyl oxygen. [c] *For* **7** and **9**, conformations suitably oriented for cis iodocyclization preclude intramolecular H bonding; MM2 minimizations are non-H-bonded.

conformational orientations in as much as **6a**, the ground-state conformation oriented toward formation of iodolactone **13**, is stabilized by 2.74 kcal/mol over **6b**, the ground-state conformation oriented toward formation of iodotetrahydrofuran **14**. Likewise **9b**, the progenitor of iodotetrahydrofuran **20**, is stabilized by 4.58 kcal/mol over **9a**, the progenitor of iodolactone **19**, and iodocyclization produces only **20**. Indeed, the diametric nucleophile selectivities obtained with **6** and **9** suggest that ground-state conformational analysis can be a useful tool in predicting group selectivity in electrophilic cyclization reactions. Apparently, the same factors that contribute to the relative energies of ground-state conformations **6a**/**6b** and **9a**/**9b** are manifest in the corresponding iodocyclization transition states.

In contrast to **6** or **9**, kinetic iodocyclization of the methyl ester of **8** (R = CH_3) produced a 52:48 mixture of iodolactone **17** and iodotetrahydrofuran **18** in 88% combined yield. Formation of both products, which are easily separable by MPLC, was anticipated on the basis of a ground-state conformational analysis since MM2 data indicated that conformers **8a** and **8b** were quite similar in energy. However, when the free acid was cyclized (**8**; R = H), only trace amounts of iodotetrahydrofuran **18** were obtained (<5%), with the major product being iodolactone **17** (76% yield). Thus, as anticipated, increasing the nucleophilicty of the -COOR functional group (-$COOCH_3$ → -COO^-Na^+) favors lactone formation from **8** (R = H).

The final substrate investigated, methylenecyclohexaneacetate **7**, was not available in pure form (see Scheme I) since MPLC purification of the aldol reaction mixture from **5** gave an inseparable 1:2 mixture of esters **6** and **7**, respectively. However, ester **6** (R = CH_3) undergoes nucleophile-specific lactonization, so we reasoned that iodocyclization of this 1:2 mixture of esters would provide clear evidence of the nucleophile selectivity of **7**; this mixture would provide three iodocyclization products if **7** were to cyclize nonselectively and only two iodocyclization products if **7** were to undergo nucleophile-specific cyclization. Prior to attempting iodocyclization of the **6**/**7** mixture, MM2 calculations predicted the latter since **7b** (R = CH_3) is stabilized by 2.93 kcal/mol relative to **7a** (R = CH_3). Indeed, cyclization gave only

Table I. Partial ^1H NMR Data for **13**, **16**, **17**, **18**, and **20**[a]

compd	$\delta(H_{1'})$	$\delta(H_2)$	$J_{1',2}$	$H_{1'},H_2$
13	2.55	2.66	12.04	trans
16	2.69	3.41	9.60	trans
17	2.65	2.89	12.15	trans
18	2.63	3.02	6.35	cis
20	2.65	2.73	10.81	trans

[a] Note: $H_{1'}$, H_2, and H_3 labels refer to the 3-hydroxybutanoate numbering system depicted in Scheme I.

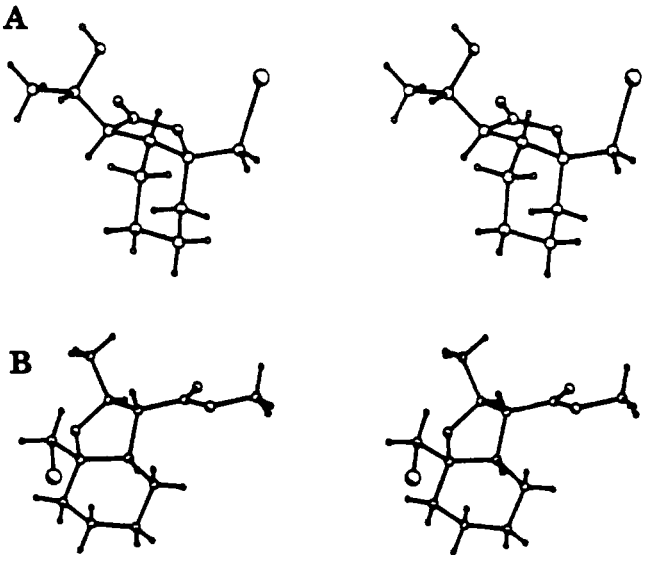


Figure 3. Computer-generated X-ray crystallographic structures for **13** (A) and **18** (B).

two products (300-MHz ^1H NMR detection), iodolactone **13** from ester **6** and iodotetrahydrofuran **16** from ester **7**.

These results with **6–9** establish that ground-state conformational analysis is a reliable qualitative indicator of nucleophile selectivity in this diastereomeric series. Nonetheless, while the observed products in these cyclizations correspond to starting material conformations (**6a**, **7b**, **8a**/**8b**, and **9b**), which place the internal nucleophile in close proximity to the C=C functional group,[14] transition-state modeling with preferred angle of attack and conformational preference with respect to partially formed bonds is required for quantitative analysis.[15]

In addition to providing a novel example of how resident stereochemistry, manifested as conformational bias, can be employed as an indicator of selectivity in iodocyclization chemistry, these results also unambiguously establish the $C_{1'},C_2$ stereochemistry of these dianionic Claisen rearrangement products. That is, by confining $H_{1'}$ and H_2 to rigid framework, reliable ^1H NMR data are made available for stereochemical analysis (Table I). Moreover, two iodocyclization products, iodolactone **13** and iodotetrahydrofuran **18**, were amenable to X-ray crystal structure analysis,[16] giving the computer-generated structures depicted in Figure 3.

Experimental Section

Melting points are uncorrected. MPLC refers to column chromatography done at 10–50 psi through EM Lobar columns packed with LiChroprep Si60 (40–63 μm) with hexane/EtOAc eluent and monitored by refractive index detection. Capillary gas chromatography (GC) was performed on a Hewlett-Packard 5890A gas chromatograph using a DB-1701 column (30 m × 0.259 mm; film thickness = 0.25 mm): initial temperatrure = 90 °C, initial time = 2 min; rate = 1 °C/min; gas pressures (psi; He, 56; N_2, 40; air, 34; H_2, 18); retention times are in minutes. The purity of all compounds was established to be >95% by ^1H NMR and GC analyses.

(±)-Methyl 2-Methylenecyclohexaneacetate (5). A 1.6 M solution of *n*-BuLi in hexane (2.62 mL, 4.20 mmol) was added dropwise to an ice-cooled solution of diisopropylamine (0.649 mL, 4.62 mmol) in THF (3 mL) under an atmosphere of dry nitrogen. After 10 min, the solution was cooled to −78 °C, and (1-cyclohexen-1-yl)methyl acetate (324 mg, 2.10 mmol) in THF (0.5 mL) was added over 5 min. After 10 min, trimethylsilyl chloride (0.587 mL, 4.62 mmol) was added in one portion, and 2 min later the dry-ice bath was removed and the solution was allowed to warm to room temperature. The solution was heated to reflux for 1.5 h and then allowed to cool to room temperature. Methanol (1 mL) was added, and the solution was stirred an additional 15 min at room temperature to cleave the silyl ester. The solution was poured into 5% aqueous NaOH (7 mL) and washed once with ether. The base layer was cooled to 0 °C and acidified with concentrated HCl and extracted several times with methylene chloride. The organic layers were collected, washed with brine, and dried (Na_2SO_4), and the solvents were removed under reduced pressure to give the acid as a light yellow oil. The crude acid was dissolved in 1 mL of ether and was added to a solution of excess diazomethane in ether at 0 °C. After 30 min, the excess diazomethane was destroyed by the addition of acetic acid until the evolution of nitrogen ceased. The solution was washed with saturated $NaHCO_3$ and brine and dried (Na_2SO_4), and the solvent was removed under reduced pressure to yield a light yellow oil. MPLC (SiO_2, 3:1 hexane/ethyl acetate) provided 181 mg (54%) of the rearranged ester **5**: IR (neat) 3082, 2933, 2856, 1741, 1646, 1281, 1263, 1236, 1170, 1120 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.0–2.0 (m, 6 H), 2.0–2.8 (m, 5 H), 3.7 (s, 3 H), 4.5 (br s, 1 H), 4.65 (br s, 1 H). Exact mass calcd for $C_{10}H_{16}O_2$: 168.1150. Found: 168.1143.

Methyl (2*R,3*R**,1′*S**)-(±)-3-Hydroxy-2-(2′-methylenecyclohexan-1′-yl)butyrate (6).** Ester **4** (750 mg, 3.78 mmol) in 1 mL of dry THF was added dropwise over 5 min to a solution of lithium diisopropylamide (11.3 mmol) in THF/hexane (15 mL/7.09 mL) cooled to −78 °C. The solution was stirred at −78 °C for 10 min, allowed to warm to room temperature, stirred for 6 h, and then heated to 50 °C for 12 h. The reaction mixture was poured into 5% aqueous NaOH (15 mL), and the ice-cooled aqueous layer was acidified with ice-cold concentrated HCl and extracted with methylene chloride (5 × 30 mL). The combined organic solutions were washed with water (45 mL) and brine (78 mL) and dried (Na_2SO_4), and the solvent was removed under reduced pressure to give a light yellow oil. The crude acid was dissolved in ice-cold ether (2 mL) and added to a solution of excess diazomethane in ether (10 mL) at 0 °C. After 30 min, the excess diazomethane was destroyed by treating the solution with acetic acid until the yellow color was quenched. The remaining solution was washed with saturated aqueous $NaHCO_3$, water, and brine dried (Na_2SO_4), and the solvent was removed under reduced pressure to give 396 mg (50%) of diastereomers **6–8** in a ratio of 94:1.5:4.5 as judged by capillary GC (retention times for **6**, 25.73; **7**, 27.15; **8**, 35.34). MPLC (SiO_2, 9:1 hexane/EtOAc) gave **6**: IR (neat) 3500–3400, 2985, 2861, 1736, 1646, 1247, 1047, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.22 (d, 3 H, J = 6.44 Hz), 1.24–1.78 (m, 7 H), 2.96–2.28 (m, 2 H), 2.74 (dd, 1 H, J = 2.55 Hz, J = 11.43 Hz), 2.84 (dt, 1 H, J = 4.09 Hz, J = 11.43 Hz), 3.64 (s, 3 H), 4.01 (dq, 1 H, J = 2.55 Hz, J = 6.44 Hz), 4.63 (br d, 2 H, J = 5.23 Hz). Exact mass calcd for $C_{12}H_{20}O_3$: 212.1412. Found: 212.1422.

Methyl (2*R,3*S**,1′*S**)-(±)- and (2*R**,3*S**,1′*R**)-(±)-3-Hydroxy-2-(2′-methylenecyclohexan-1′-yl)butyrate (8 and 9).** To a solution of LDA (1.14 mmol) in dry THF/hexane (4.0 mL/0.312 mL) at −78 °C under dry nitrogen was added dropwise over 2 min a solution of ester **5** (150 mg, 0.893 mmol) in 1.0 mL of THF. After 15 min, acetaldehyde (1.14 mmol) was added in one portion, and the solution was stirred for an additional 10 min at −78 °C. The reaction was quenched at −78 °C by the addition of a solution of acetic acid (1.0 mL) in THF (1.0 mL) and then warmed to room temperature. The solution was carefully poured into saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (3 × 10 mL). The collected organic layers were washed with water (1×) and brine (1×) and dried (Na_2SO_4), and the solvents were removed under reduced pressure to provided β-hydroxy esters **6–9** in a ratio determined by capillary GC to be 3.7:6.9:38.7:50.7 **6**/**7**/**8**/**9** (retention times for **6**, 25.73; **7**, 27.15, **8**, 35.34; **9**, 32.40). MPLC (SiO_2, 9:1 hexane/EtOAc) provided esters **6** and **7** as an inseparable mixture of diastereomers (15.1 mg, 8.0%), ester **8**, and ester **9**. **8** (55.3 mg, 29.2%): IR (neat) 3455, 3072, 2934, 2881, 1738, 1646, 1437, 1233, 1165, 895 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.79–0.86 (m, 2 H), 1.26 (d, 3 H, J = 6.43 Hz), 1.5–1.65 (m, 4 H), 2.03–2.34 (m, 3 H), 2.55 (m, 1 H), 3.03 (dd, 1 H,

(14) For a discussion of reactivity as a function of time and proximity, see: Menger, F. M. *Acc. Chem. Res.* **1985**, *18*, 128.

(15) For a discussion of theoretical investigations of transition structures, see: Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G.; Wu, Y.-D.; Brown, F. K.; Spellmeyer, D. C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science* **1986**, *231*, 1108–17.

(16) Complete X-ray crystalographic data for iodolactone **13** and iodotetrahydrofuran **18** respectively, are available as supplementary material: space group, *Pcab* (*cba* of *Pbca* (No. 61)), $P2_1/n$; lattice, orthorhombic, monoclinic; Z, 8, 4; a (Å), 10.715 (3), 11.506 (2); b (Å), 13.286 (2), 8.898 (1); c (Å), 17.013 (4), 13.127 (1); β (deg), no value, 98.85 (1).

J = 5.89 Hz, J = 11.10 Hz), 3.62 (s, 3 H), 4.13 (m, 1 H), 4.60 (s, 1 H), 4.64 (br s, 1 H). Exact mass calcd for $C_{12}H_{20}O_3$: 212.1412. Found: 212.1420. **9** (72.1 mg, 38.3%): IR (neat) 3463, 3071, 2934, 2859, 1734, 1646, 1439, 1169, 926 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, 3 H, J = 6.29 Hz), 1.33–1.63 (m, 4 H), 1.75–1.79 (m, 2 H), 2.17 (dd, 2 H, J = 3.24, J = 8.71), 2.55 (br s, 1 H), 2.67 (br dt, 1 H, J = 11.03 Hz), 3.00 (dd, 1 H, J = 6.24, J = 11.03 Hz), 3.69 (s, 3 H), 3.93 (m, 1 H, J = 6.26), 4.78 (br s, 1 H), 4.83 (br s, 1 H). Exact mass calcd for $C_{12}H_{20}O_3$: 212.1413. Found: 212.1420.

(2*R,3*S**,1′*R**)-(±)-2-(2′-Methylenecyclohexan-1′-yl)-1,3-butanediol. General Procedure A.** To a stirred suspension of $LiAlH_4$ (16.0 mg, 0.61 mmol) in ether (2.5 mL) at −78 °C was added dropwise over 2–3 min a solution of methylenecyclohexaneacetate **6** (**6**/**7**, 98/2, 84 mg, 0.40 mmol) in ether (0.5 mL). The mixture was stirred for an additional 10 min at −78 °C and then allowed to warm to room temperature and stirred for 12 h. Water (3 drops) was added cautiously followed by 15% aqueous NaOH (3 drops), and the resulting mixture was stirred vigorously for 15 min. Filtration and removal of the solvent under reduced pressure provided (2*R**,3*S**,1′*R**)-(±)-2-(2′-methylenecyclohexan-1′-yl)-1,3-butanediol (71 mg, 97%), which was used in the next step without further purification: IR (CCl_4) 3378, 3071, 2932, 2860, 1646, 1465, 1456, 1060 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.7–2.6 (m, 11 H), 1.35 (d, 3 H, J = 6 Hz), 2.6–3.0 (m, 1 H), 3.7–4.3 (m, 3 H), 4.75 (br s, 2 H). Exact mass calcd for $C_{11}H_{20}O_2$: 184.1463. Found: 184.1462.

(2*R,3*S**,1′*S**)-(±)-2-(2′-Methylenecyclohexan-1′-yl)-1,3-butanediol.** Methylenecyclohexaneacetate **8** (68 mg, 0.32 mmol) was converted to (2*R**,3*S**,1′*S**)-(±)-2-(2′-methylenecyclohexan-1′-yl)-1,3-butanediol (52 mg, 88%) according to general procedure A and used in the next step without further purification: IR (CCl_4) 3352, 3071, 2934, 2860, 1647, 1454, 1034 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.6–2.2 (m, 9 H), 1.1 (d, 3 H, J = 7 Hz), 3.4 (br d, 2 H, J = 7 Hz), 3.7–4.4 (m, 3 H), 4.4 (br s, 1 H), 4.5 (br s, 1 H). Exact mass calcd for $C_{11}H_{20}O_2$: 184.1463. Found: 184.1470.

(2*R,3*R**,1′*S**)-(±)-2-(2′-Methylenecyclohexan-1′-yl)-1,3-butanediol.** Methylenecyclohexaneacetate **9** (47.5 mg, 0.224 mmol) was converted to (2*R**,3*R**,1′*S**)-(±)-2-(2′-methylenecyclohexan-1′-yl)-1,3-butanediol (37 mg, 90%) according to general procedure A and used in the next step without further purification: IR (CCl_4) 3363, 3072, 2933.1, 2859, 1646, 1065 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.7–2.6 (m, 9 H), 1.25 (d, 3 H, J = 8 Hz), 3.4 (br s, 2 H), 3.6–4.2 (m, 3 H), 4.6 (br s, 1 H), 4.7 (br s, 1 H). Exact mass calcd for $C_{11}H_{20}O_2$: 184.1463. Found: 184.1462.

(4*R,5*S**,1′*S**)-(±)-2,2,4-Trimethyl-5-(2′-methylenecyclohexan-1′-yl)-1,3-dioxane (10). General Procedure B.** The crude diol prepared from ester **6**, 2,2-dimethoxypropane, and *p*-toluenesulfonic acid monohydrate was dissolved in benzene (10 mL) and refluxed under a Soxhlet extractor containing freshly conditioned 4-Å molecular sieves for 3 h. Anhydrous K_2CO_3 was added to the cooled reaction mixture and the mixture stirred at room temperature for 4 h. The mixture was next filtered, and the solvents were removed under reduced pressure. The remaining oil was redissolved in ether, washed with water and brine, and dried (Na_2SO_4), and the solvents were removed under reduced pressure. The product was purified by MPLC (9:1 hexane/EtOAc) to give dioxane **10** (62 mg, 84%): IR (neat) 3069, 2986, 2932, 2858, 1653, 1456, 1381, 1200, 1226, 1180, 1049 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17–2.20 (m, 10 H), 1.23 (d, 3 H, J = 6.14 Hz), 1.36 (s, 3 H), 1.39 (s, 3 H), 3.59 (dd, 1 H, J = 8.40 Hz, J = 11.92 Hz), 3.66 (dd, 1 H, J = 5.20, J = 11.92), 3.79 (dq, 1 H, J = 6.14 Hz, J = 8.68 Hz), 4.63 (br s, 1 H), 4.73 br s, 1 H). Exact mass calcd for $C_{14}H_{24}O_2$: 224.1776. Found: 224.1770.

(4*R,5*R**,1′*R**)-(±)-2,2,4-Trimethyl-5-(2′-methylenecyclohexan-1′-yl)-1,3-dioxane (11).** Following general procedure B, the diol prepared from the ester **8** (47 mg, 0.19 mmol) was converted to dioxane **11** (10 mg, 20% yield): IR (neat) 3070, 2932, 2861, 1647, 1456, 1381, 1260, 1196, 1122, 1061 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17–2.65 (m, 10 H), 1.26 (d, 3 H, J = 6.77 Hz), 1.38 (s, 3 H), 1.39 (s, 3 H), 3.63 (dd, 1 H, J = 5.72 Hz, J = 11.7 Hz), 3.66 (dd, 1 H, J = 5.20, J = 11.7), 4.24 (dq, 1 H, J = 6.77 Hz, J = 3.47 Hz), 4.73 (br d, 2 H). Exact mass calcd for $C_{14}H_{24}O_2$: 224.1776. Found: 224.1784.

(4*R,5*R**,1′*S**)-(±)-2,2,4-Trimethyl-5-(2′-methylenecyclohexan-1′-yl)-1,3-dioxane (12).** Following general procedure B, the diol prepared from the ester **9** (35 mg, 0.19 mmol) was converted to dioxane **12** (38 mg, 90% yield): IR (neat) 3080, 2991, 2933, 2858, 1641, 1448, 1379, 1251, 1193, 1130, 1064, 980 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13–1.77 (m, 6 H), 1.19 (d, 3 H, J = 6.58 Hz), 2.03–2.20 (m, 6 H), 2.34 (br dt, 1 H), 2.42 (m, 1 H), 4.00 (dd, 1 H, J = 2.60 Hz, J = 12.12 Hz), 4.06 (dd, 1 H, J = 3.77 Hz, J = 12.12 Hz), 4.29 (dq, 1 H, J = 3.58 Hz, J = 6.58 Hz), 4.43 (br s, 1 H), 4.72 (br s, 1 H). Exact mass calcd for $C_{14}H_{24}O_2$: 224.1776. Found: 224.1792.

(3α,3a*β*,7a*β*,1′*R)-(±)-Hexahydro-3-(1′-hydroxyethyl)-7a-(iodomethyl)-2(3*H*)-benzofuranone (13). General Procedure C.** Methylenecyclohexaneacetic acid **6** (R = H; 348 mg, 1.76 mmol) was dissolved in saturated aqueous $NaHCO_3$ (10 mL) and treated with a solution of iodine (450 mg, 1.76 mmol) in methylene chloride (10 mL). The resulting two-phase mixture was stirred at room temperature for 1 h at which time the remaining iodine was destroyed by dropwise addition of aqueous Na_2SO_3. The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic solutions were washed with water and brine, dried (Na_2SO_4), and filtered, and the solvents were removed under reduced pressure to give a yellow solid, which was recrystallized from ether to provide iodolactone **13** (497 mg, 87%) as colorless crystals: IR (KBr pellet) 3446, 2936, 2854, 1751, 1239, 1190, 1170, 1008, 965 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (d, 2 H, J = 6.33 Hz), 1.0–1.8 (m, 6 H), 1.89 (br d, 1 H, J = 14.82 Hz), 2.24 (br d, 1 H, J = 14.06 Hz), 2.55 (dd, 1 H, J = 3.60 Hz, J = 12.04 Hz), 2.66 (dd, 1 H, J = 6.11 Hz, J = 12.04 Hz), 3.43 (d, 1 H, J = 3.57 Hz), 3.55 and 3.62 (2 d's, 2 H, J = 11.57 Hz), 3.92–4.05 (m, 1 H). Anal. Calcd for $C_{11}H_{17}O_3I$: C, 40.78; H, 5.29; I, 39.17. Found: C, 40.56; H, 5.14; I, 39.00.

Identical reaction conditions were employed with the methyl ester of **6** (R = CH_3; 53 mg, 0.25 mmol), again giving only iodolactone **13** (64 mg, 79%). There was no evidence for the carboxylic acid of **14** (R = H) in the crude reaction mixture.

(2α,3*β*,3aα,7aα)-(±)-Octahydro-3-carbomethoxy-7a-(iodomethyl)-2-methylbenzofuran (16; R = CH_3). As in procedure C, iodocyclization of methyl ester **7** (1:2 **6**/**7** mixture; R = CH_3; 31 mg, 0.15 mmol) followed by MPLC (SiO_2, 3:1 hexane/EtOAc) gave, in order of elution, iodotetrahydrofuran **16** (from **7**; 30 mg, 0.088 mmol, 87%) and iodolactone **13** (from **6**; 14 mg, 0.042 mmol, 85%). **16**: IR (neat) 2936, 2862, 1738, 1454, 1232, 1174, 1052, 1024 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05–1.91 (m, 8 H), 1.12 (d, 3 H, J = 6.38 Hz), 2.69 (br m, 1 H, J = 9.60 Hz), 3.42 (dd, 1 H, J = 9.60 Hz, J = 9.45 Hz), 3.46 (d, 1 H, J = 10.93 Hz), 3.49 (d, 1 H, J = 10.93 Hz), 3.69 (s, 3 H), 4.45 (dq, 1 H, J = 9.45 Hz, J = 6.38 Hz). Exact mass calcd for $C_{12}H_{19}O_3I$: 338.0381. Found: 338.0381.

(3α,3a*β*,7a*β*,1′*S)-(±)-Hexahydro-3-(1′-hydroxyethyl)-7a-(iodomethyl)-2(3*H*)-benzofuranone (17) and (2α,3aα,7aα)-(±)-Octahydro-3-carbomethoxy-7a-(iodomethyl)-2-methylbenzofuran (18; R = CH_3).** As in procedure C, iodocyclization of methyl ester **8** (R = CH_3, 28 mg, 0.132 mmol) followed by MPLC (SiO_2, 3:1 hexane/EtOAc) gave, in order of elution, iodotetrahyrofuran **18** (R = CH_3, 19 mg, 0.056 mmol, 43%) and iodolactone **17**. (**19** mg, 0.059 mmol, 45%). **18**: IR (neat) 2937, 2884, 1735, 1456, 1407, 1272, 1175, 1090, 1021, cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00–1.95 (m, 6 H), 1.32 (d, J = 6.2 Hz), 2.63 (dt, 1 H, J = 6.4 Hz), 3.02 (dd, 1 H, J = 6.35 Hz, J = 9.17 Hz), 4.54 (dq, 1 H, J = 6.2 Hz J = 9.17 Hz). Anal. Calcd for $C_{12}H_{19}O_3I$: C, 42.62; H, 5.66; I, 37.53. Found: C, 42.43; H, 5.68; I, 37.52. **17**: IR (neat) 3476, 2938, 2865, 1761, 1454, 1254, 1170, 1012, 962 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82–1.89 (m, 7 H), 1.32 (d, 3 H, J = 6.36 Hz), 2.23 (dm, 1 H), 2.65 (br dd, 1 H), 2.73 (br s, 1 H), 2.89 (dd, 1 H, J = 4.34 Hz, J = 12.15 Hz), 3.54 (d, 1 H, J = 11.6 Hz), 3.59 (d, 1 H, J = 11.6 Hz), 4.20 (m, 1 H). Exact mass calcd for $C_{11}H_{17}O_3I$: 324.0225. Found: 324.0187. Anal. Calcd for $C_{11}H_{17}O_3I$: C, 40.78; H, 5.29; I, 39.17. Found: C, 41.00; H, 5.36; I, 39.51.

Identical reaction conditions were employed with the carboxylic acid of **8** (R = H), this time giving iodolactone **17** (300 mg, 76%). There was evidence for a trace (<5%) of the carboxylic acid of iodotetrahydrofuran **18** in the crude reaction mixture.

(2α,3α,3a*β*,7a*β*)-(±)-Octahydro-3-carbomethoxy-7a-(iodomethyl)-2-methylbenzofuran (20; R = CH_3). As in procedure C, iodocyclization of methyl ester **9** (35 mg, 0.165 mmol) followed by MPLC (SiO_2, 4:1 hexane/EtOAc) gave iodotetrahydrofuran **20** (R = CH_3, 49.3 mg, 88%): IR (neat) 2937, 2862, 1739, 1453, 1436, 1308, 1265, 1177, 1091, 1021, 964 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15–1.68 (m, 7 H), 1.31 (d, 3 H, J = 6.07 Hz), 1.83–1.89 (m, 1 H), 2.65 (dt, 1 H, J = 3.92 Hz, J = 10.8 Hz), 2.73 (dd, 1 H, J = 8.76 Hz, J = 10.8 Hz), 3.39 (d, 1 H, J = 10.79 Hz), 3.42 (d, 1 H, J = 10.79 Hz), 3.68 (s, 3 H), 4.22 (dq, 1 H, J = 6.07 Hz, J = 8.76 Hz). Exact mass calcd for $C_{11}H_{16}O_2I$ (M − OCH_3): 307.0194. Found: 307.0182.

(2α,3α,3a*β*,7a*β*)-(±)-Octahydro-7a-(iodomethyl)-2-methylbenzofuran-3-carboxylic Acid (20; R = H). As in procedure C, iodocyclization of methylenecyclohexaneacetic acid **9** (R = H; 73 mg, 0.369 mmol) gave iodotetrahydrofuran **20** (R = H) when the workup was modified as follows. The organic and aqueous layers were separated. The aqueous layer was cooled to 0 °C and acidified carefully with concentrated HCl, and iodotetrahydrofuran **20** was extracted into methylene chloride. The combined organic solutions were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Recrystallization of the resulting material gave iodotetrahydrofuran **20** (R = H; 83 mg, 66%): IR ($CDCl_3$) 3500, 2600, 2937, 2863, 1707, 1687, 1656, 1556, 1094 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.1–2.0 (m, 7 H), 1.41 (d, 3 H, J = 6.10 Hz), 2.36 (m, 1 H), 2.73 (m, 1 H), 2.82 (dd, 1 H, J = 11.3 Hz), 3.43

(d, 1 H, J = 10.8 Hz), 3.51 (d, 1 H, J = 10.8 Hz), 4.29 (dq, 1 H, J = 6.10 Hz), 10.3 (br s, 1 H). Anal. Calcd for $C_{11}H_{17}O_3I$: C, 40.78; H, 5.29; I, 39.17. Found: C, 41.02; H, 5.38; I, 38.82.

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Supplementary Material Available: X-ray crystallographic data for iodolactone **13** and iodotetrahydrofuran **18** (6 pages). Ordering information is given on any current masthead page.

An Enantioselective Central-Axial-Central Chiral Element Transfer Process Leading to a Concise Synthesis of (+)-Sterpurene: Intramolecular Diels-Alder Reactions of Vinylallene Sulfoxides[1a,b]

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Abstract: The intramolecular Diels-Alder (IMDA) reaction of vinylallene sulfoxide **19** as the diene component occurs in a rapid and stereoselective manner at room temperature to give tricyclic **20** in good yield. Sulfoxide **19** cyclizes ~140 times faster than the corresponding hydrocarbon **15a**. It was also shown that *gem*-dimethyl substitution on the tether linking the vinylallene and vinyl group accelerates the rate of cyclization by only a factor of ~2.6. Treatment of enantiomerically enriched diene propargyl alcohol **6** with benzenesulfenyl chloride gave vinylallene sulfoxide **4** which cyclized in a highly enantio- and diastereoselective fashion to afford optically active tricyclic sulfoxide **5**. Sulfoxide **5** was converted in two steps to the novel sesquiterpene fungal metabolite (+)-sterpurene, thus establishing its absolute configuration. By use of 2D NMR techniques, most of the proton and carbon signals in the ^1H and ^{13}C NMR spectra of sterpurene (**8**) and the precursor diene **33** were assigned.

The intramolecular Diels-Alder (IMDA) reaction has been the subject of numerous synthetic and mechanistic studies,[2] but there has been a relative paucity of work on the vinylallene[3] variant of this reaction.[4] Although the intermolecular[5] vinylallene Diels-Alder reaction appears to have been first reported in 1960, the first definitive example of a vinylallene IMDA reaction was not reported until 1982.[4a] Inspection of Dreiding models of the hydrindane precursor **1** and the decalin precursor **2** (Scheme I) suggests that the cyclization of **1** should be considerably more facile than that of **2** due to the distorted overlap and eclipsing interactions present in the conformation of **2** leading to the decalin system **3b**. In contrast, there is excellent overlap (and no eclipsing interactions) in the conformation of **1** leading to the hydrindane system **3a**. Moreover, because of the shorter tether in **1** compared to that in **2**, cyclization of **1** should be entropically facilitated. A brief inquiry into this matter by Snider suggests that the cyclization of a vinylallene system to give a hydrindane is more facile than that of the homologous vinylallene leading to the decalin system.[4c,6]

Scheme I

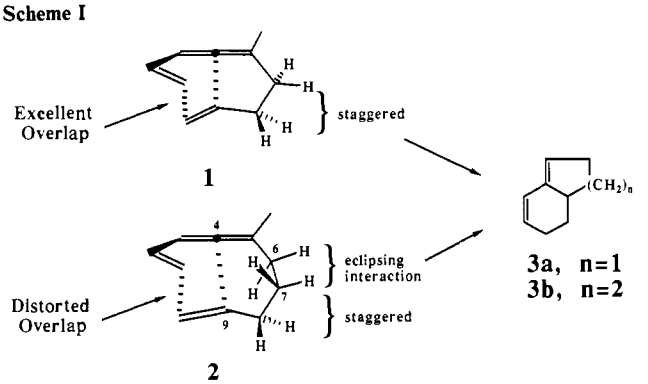
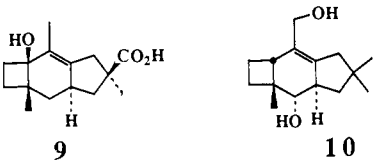


Chart I



(1) (a) A preliminary account of this paper has appeared. See: Gibbs, R. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 4062. (b) This paper is taken in part from the Ph.D. Dissertation of R. A. Gibbs, University of California, Riverside, CA, August 1988. (c) Analytical Chemical Instrument Facility, UC Riverside.

(2) For reviews, see: (a) Craig, D. *Chem. Soc. Rev.* **1987**, *16*, 187. (b) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. (c) Ciganek, E. *Org. React.* **1984**, *32*, 1.

(3) For reviews of the chemistry of vinylallenes, see: (a) Egenburg, I. Z. *Russ. Chem. Rev.* **1978**, *47*, 470. (b) Okamura, W. H. *Acc. Chem. Res.* **1983**, *16*, 81.

(4) Vinylallene IMDA reactions: (a) Deutsch, E. A.; Snider, B. B. *J. Org. Chem.* **1982**, *47*, 2682. (b) Deutsch, E. A.; Snider, B. B. *Tetrahedron Lett.* **1983**, *24*, 3701. (c) Snider, B. B.; Burbaum, B. W. *J. Org. Chem.* **1983**, *48*, 4370. (d) Reich, H. J.; Eisenhart, E. K. *J. Org. Chem.* **1984**, *49*, 5282. (e) Reich, H. J.; Eisenhart, E. K.; Olson, R. E.; Kelly, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 7791. (f) Keck, G. E.; Kachensky, D. F. *J. Org. Chem.* **1986**, *51*, 2487. Iwai (ref 4g; and later Ollis, ref 4h) proposed that certain cyclization reactions proceeded via a vinylallene IMDA, but later studies by Garratt and Neoh (ref 4i) showed that these reactions proceeded via a stepwise, biradical mechanism: (g) Iwai, I.; Ide, J. *Chem. Pharm. Bull.* **1964**, *12*, 1094. (h) Bartlett, A. J.; Laird, T.; Ollis, W. D. *J. Chem. Soc., Perkin Trans 1* **1975**, 1315. (i) Garratt, P. J.; Neoh, S. B. *J. Org. Chem.* **1979**, *44*, 2667. Intramolecular Diels-Alder reactions of *allenes* as dienophiles are also known: (j) Hayakawa, K.; Yasukouchi, T.; Kanematsu, K. *Tetrahedron Lett.* **1987**, *28*, 5895. (k) Hayakawa, K.; Ohsuki, S.; Kanematsu, K. *Tetrahedron Lett.* **1986**, *27*, 4205. (l) Himbert, G.; Fink, D. *Tetrahedron Lett.* **1985**, *26*, 4363. (m) Saxton, H. M.; Sutherland, J. K.; Whaley, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1449. (n) For a biosynthetic proposal involving a vinylallene IMDA, see: Schreiber, S. L.; Kiessling, L. L. *J. Am. Chem. Soc.* **1988**, *110*, 631; *Tetrahedron Lett.* **1989**, *30*, 433.

(5) Intermolecular vinylallene Diels-Alder reactions: (a) Jones, E. R. H.; Lee, H. H.; Whiting, M. C. *J. Chem. Soc.* **1960**, 341. (b) For other examples, see ref 3a. (c) For a recent paper, see: Reich, H. J.; Eisenhart, E. K.; Whipple, W. L; Kelly, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 6432.

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