Quantitative Analyses of the Four Isomers of 3,4-Diphenylcyclopentene by Chiral Gas Chromatography

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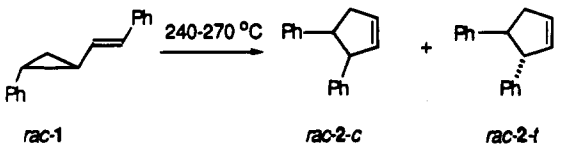
The four isomers of 3,4-diphenylcyclopentene are well resolved by chiral gas chromatography on a Cyclodex B column, eluting in the ordered sequence (3*S*,4*R*), (3*R*,4*S*), (3*S*,4*S*), and (3*R*,4*R*). Absolute stereochemical assignments were made through chemical correlations relating the 3,4-diphenylcyclopentenes with a known reference compound, (1*S*,2*S*)-(+)-*cis*-2-phenylcyclopentanol.

Introduction

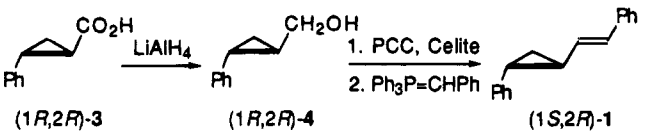
The thermal isomerization of *trans*-1-((*E*)-styryl)-2-phenylcyclopropane (*rac*-**1**) at 240–270 °C leads to a 1:3 mixture of the cis and trans isomers of 3,4-diphenylcyclopentene (*rac*-**2**-*c* and *rac*-**2**-*t*).[1]



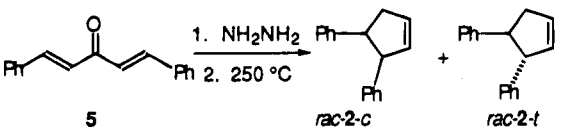
We anticipated that a thorough kinetic and stereochemical investigation of these rearrangements might provide useful information relevant to substituent effects on vinylcyclopropane-to-cyclopentene [1,3] carbon sigmatropic shifts,[2,3] so a sensitive method for quantitative analyses of submilligram samples containing all four isomers of 3,4-diphenylcyclopentene was sought. For such samples, preparative chromatography might well separate the cis and trans diastereomers, but traditional polarimetric methods for estimating enantiomeric excess (ee) values of cis and trans isomers would probably not be efficacious. Chiral gas chromatography,[4] it was hoped, would prove a useful alternative, both to analyze the diphenylcyclopentenes and to aid in making the required correlations of absolute stereochemistry.

Results

trans-1-((*E*)-Styryl)-2-phenylcyclopropane (*rac*-**1**)[1,5,6] may be prepared from *trans*-2-phenylcyclopropanecarboxylic acid through a reduction with $LiAlH_4$ to give the corresponding alcohol,[7] which upon oxidation by pyridinium chlorochromate[8] affords *trans*-2-phenylcyclopropanecarboxaldehyde. Condensation of this aldehyde with benzylidene triphenylphosphorane in a Wittig olefination[9] gives the desired vinylcyclopropane along with some *Z* olefin, isomers which may be separated by HPLC. (1*S*,2*R*)-*trans*-1-((*E*)-Styryl)-2-phenylcyclopropane ((1*S*,2*R*)-**1**) was synthesized by this same route from (1*R*,2*R*)-**3**.[10]



Racemic samples of *cis*- and *trans*-3,4-diphenylcyclopentenes, *rac*-**2**-*c* and *rac*-**2**-*t*, were prepared from dibenzylideneacetone following the synthesis reported by Shoppee and Henderson.[11]



It was found that the enantiomers of *rac*-**2**-*c* and *rac*-**2**-*t* were base-line resolvable on a Cyclodex B capillary column at 165 °C and easily separated, with the **2**-*c* enantiomers eluting first. Heating a sample of (1*S*,2*R*)-**1** of 87% ee led to enantiomerization of this starting material, formation of some *cis*-1-((*E*)-styryl)-2-phenylcyclopropane, and rearrangement to a few percent of the 3,4-diphenylcyclopentenes. These cyclopentenes were shown by chiral GC to be nonracemic, for the first-to-elute enantiomer of both **2**-*c* and **2**-*t* was more prominent than the second (Figure 1). Thus, the resolution problem was solved, and the fact that the vinylcyclopropane

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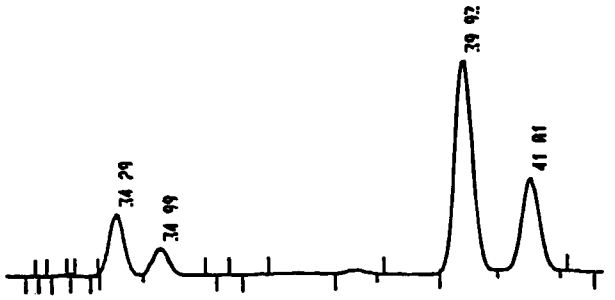
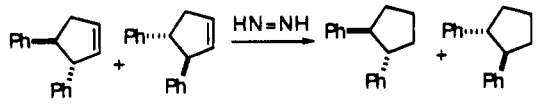


Figure 1. Chiral GC resolution on a Cyclodex B column of nonracemic mixtures of cyclopentenes **2-*c*** and **2-*t*** from a thermal isomerization of (1*S*,2*R*)-**1**.

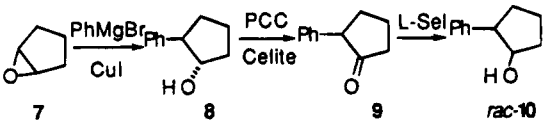
rearrangement of (1*S*,2*R*)-**1** does give nonracemic cyclopentene products at low conversions, even as the vinylcyclopropane reactant undergoes kinetically competitive thermal enantiomerization and cis,trans equilibration reactions, was established.

The only remaining requirement set by the methodological objectives of this study was correlation of absolute stereochemistry with order of elution for the four cyclopentene products on the chiral GC column.

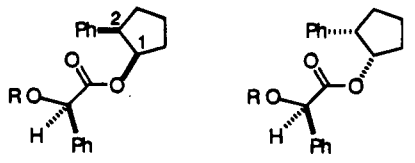
A diimide reduction of a chiral sample of **2-*t*** (20% ee by chiral GC) from a thermal rearrangement of (1*S*,2*R*)-**1** gave a mixture of the enantiomers of *trans*-1,2-diphenylcyclopentane;[12] these enantiomers could be resolved by chiral GC and were found to be present in a 59:41 ratio (18% ee), with the early-eluting enantiomer the more prominent. Thus, an authentic chiral sample of *trans*-1,2-diphenylcyclopentane of known absolute stereochemistry would serve to establish the absolute stereochemistry of the two **2-*t*** enantiomers.



A sample of (1*R*,2*R*)-*trans*-1,2-diphenylcyclopentane ((1*R*,2*R*)-**6**) was prepared to provide that essential reference compound. Racemic *cis*-2-phenylcyclopentanol (*rac*-**10**) was synthesized from cyclopentene oxide (**7**), through addition of phenylmagnesium bromide in the presence of CuI in THF,[13] oxidation of the intermediate *trans*-2-phenylcyclopentanol (**8**)[14] with PCC on Celite, and reduction of 2-phenylcyclopentanone (**9**)[15] with lithium tri-*sec*-butyl borohydride (L-Selectride, Aldrich).[16] This sterically demanding hydride reagent gave the cis alcohol *rac*-**10** with high stereoselectivity; *trans*-2-phenylcyclopentanol was not detected by gas chromatography in the reaction mixture.



Resolution of *rac*-**10** was achieved by way of the derived diastereomeric mandelate esters.[17] The (*R*)-*O*-acetylmandelates (1*R*,2*R*)-**11a** and (1*S*,2*S*)-**11a** were formed under mild and essentially neutral conditions from (*R*)-*O*-acetylmandelic acid in CH_2Cl_2 using dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP); they were selectively hydroylzed to (*R*)-mandelates (1*R*,2*R*)-**11b** and (1*S*,2*S*)-**11b** with aqueous NaSH at pH 8.



Recrystallization of the mandelate ester mixture gave a single diastereomer, (1*R*,2*R*)-**11b**, which upon hydrolysis afforded the cis alcohol (1*R*,2*R*)-**10** as a clear colorless liquid: $[\alpha]_D$ −73.6° (*c* 0.38, $CHCl_3$) [lit.[18] $[\alpha]_D$ −90.4° (no solvent cited)]. The sample of (1*R*,2*R*)-**10** from hydrolysis of the recrystallized mandelate ester (1*R*,2*R*)-**11b** was optically pure according to a chiral GC determination on a Lipodex E column.

Hydrolysis of the mother liquor from the recrystallization of the mixture of (1*R*,2*R*)-**11b** and (1*S*,2*S*)-**11b** gave a sample of cis alcohol enriched in the other enantiomer, (1*S*,2*S*)-**10**, of 29% ee by chiral GC; it was converted to the tosylate ester,[19] and the tosylate group was displaced with a higher order cuprate reagent, $Ph_2Cu(CN)Li_2$,[20] to give (1*R*,2*R*)-**6** along with 1-phenylcyclopentene, the major product.

The (1*R*,2*R*)-**6** prepared from (1*S*,2*S*)-**12** was purified by repeated preparative GC and was found by chiral GC to be of 30% ee, with the second-eluting enantiomer predominant (Figure 2). Since the chiral sample of **6** obtained from the trans cyclopentene product **2-*t*** derived

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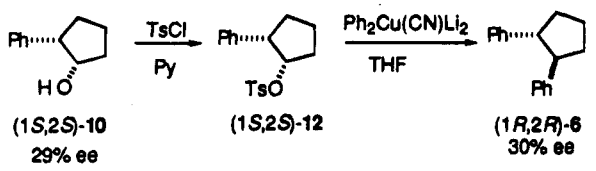
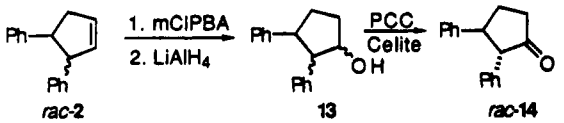


from the thermal reaction of (1*S*,2*R*)-**1** contained an excess of the first-to-elute (1*S*,2*S*)-**6** enantiomer (Figure 2), the major trans product from the thermal vinylcyclopropane-to-cyclopentene rearrangement of (1*S*,2*R*)-**1** is (3*S*,4*S*)-*trans*-3,4-diphenylcyclopentene, (3*S*,4*S*)-**2**-*t*. The elution order for the *trans*-1,2-diphenylcyclopentanes on the Cyclodex B column is (1*S*,2*S*)-**6** before (1*R*,2*R*)-**6**, and the *trans*-3,4-diphenylcyclopentenes elute on this column in the order (3*S*,4*S*)-**2**-*t* before (3*R*,4*R*)-**2**-*t*.

A chiral version of *trans*-2,3-diphenylcyclopentanone (**14**) was selected as a convenient reference to correlate chiral GC retention times and absolute stereochemical assignments for the (3*S*,4*R*)-**2**-*c* and (3*R*,4*S*)-**2**-*c* enantiomers. The racemic ketone is well characterized,[21] and a nonracemic sample might be derived from nonracemic samples of both **2**-*t* and **2**-*c*.

Racemic *trans*-2,3-diphenylcyclopentanone (*rac*-**14**) was synthesized from a mixture of racemic **2**-*c* and **2**-*t* (*rac*-**2**) to confirm the projected reaction sequence and to provide a sample to test for chiral GC separation of its enantiomers. An initial attempt to achieve this conversion involved reduction of *rac*-**2** with diborane in THF followed by H_2O_2 oxidation in aqueous base[22] and then oxidation with Jones reagent;[23] the mixture of *rac*-**14** and the cis and trans isomers of 3,4-diphenylcyclopentanone[24] obtained proved difficult to separate by preparative GC. A far more convenient three-step procedure was then implemented, involving epoxidation of the double bond, opening the epoxide with a hydride reagent to give a mixture of 2,3-diphenylcyclopentanols (**13**), and oxidation of the resulting alcohol functionality to give the racemic trans ketone *rac*-**14**.



Chiral GC resolution of the enantiomers of ketone *rac*-**14** was successful. The enantiomers were base-line resolved using either the Cyclodex B (150 °C isothermal) or, more conveniently, a Lipodex E (165 °C isothermal) capillary column.

The *cis*- and *trans*-cyclopentene products from thermal rearrangement of a 300-mg sample of (1*S*,2*R*)-**1** were isolated and purified by preparative GC; they were each then subjected to the three-step sequence to give the stereochemically related 2,3-diphenylcyclopentanones.

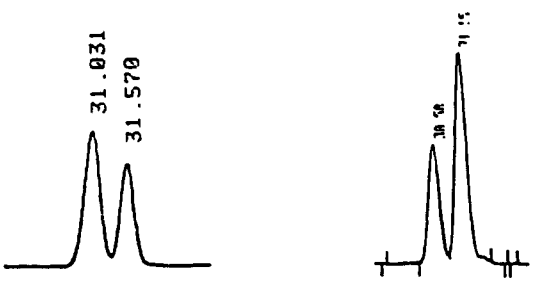
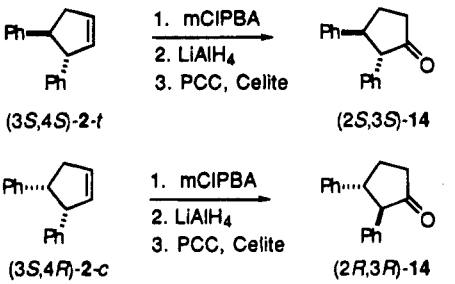


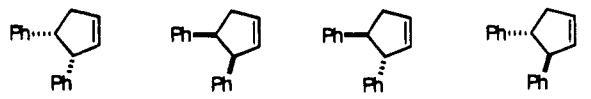
Figure 2. Chiral GC resolution on a Cyclodex B column of the *trans*-1,2-diphenylcyclopentane enantiomers secured through diimide reduction of (3*S*,4*S*)-**2**-*t* (20% ee) formed from (1*S*,2*R*)-**1** (a) and from (1*S*,2*S*)-**10** (29% ee) (b).



Chiral GC analysis of ketone **14** from *trans*-3,4-diphenylcyclopentene (3*S*,4*S*)-**2**-*t* (9% ee) showed it to be of 9% ee, with the later-eluting peak predominant; thus, the later-eluting enantiomer is (2*S*,3*S*)-**14**. Chiral GC analysis of ketone **14** obtained from the optically active *cis*-3,4-diphenylcyclopentene thermal product from (1*S*,2*R*)-**1** (8% ee) showed it to be of 10% ee, with the early-eluting peak predominant; thus, the ketone is predominantly (2*R*,3*R*)-**14**. The major cis cyclopentene product from the thermal rearrangement of (1*S*,2*R*)-**1** thus is (3*S*,4*R*)-**2**-*c*.

Conclusions

All four 3,4-diphenylcyclopentenes may be separated by chiral GC using a capillary Cyclodex B column, and the elution order has been demonstrated. The cis isomers come first, with (3*S*,4*R*)-**2**-*c* eluting before (3*R*,4*S*)-**2**-*c*, followed by the trans enantiomers, with (3*S*,4*S*)-**2**-*t* coming before (3*R*,4*R*)-**2**-*t*; from left to right, these structures now correlate with the chiral GC retention order sequence shown in Figure 1 above.



The stereochemical determinations employed to establish these assignments were based on chemical correlations linked to *cis*-2-phenylcyclopentanols of known absolute stereochemistry, with chiral GC used as a convenient qualitative and quantitative probe of enantiomeric excess values; these correlations are summarized in Scheme 1 for one set of stereochemically related compounds.

While the relative magnitudes of the four rate constants for thermal isomerizations leading from (1*S*,2*R*)-**1** to the four isomers of 3,4-diphenylcyclopentene cannot be inferred from the present results—rather detailed kinetic work and analyses would be required to sort through the complex set of competing first-order pro-

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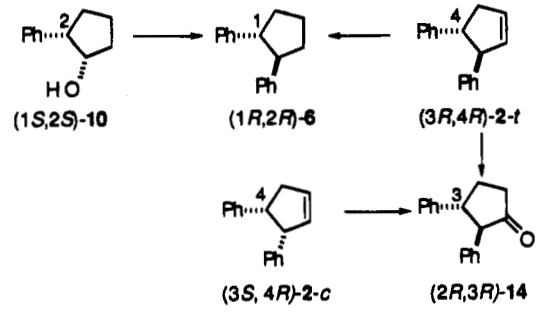
Scheme 1



cesses contributing to the overall stereochemical outcomes—a preliminary, conditional, and qualitative assessment of reaction stereochemistry may be made. If the 3,4-diphenylcyclopentenes formed directly from the *cis*-1-((*E*)-styryl)-2-phenylcyclopropane enantiomers formed as the thermal isomerizations of (1*S*,2*R*)-**1** proceed are of only secondary significance, and the observed ratios of isomers do reflect qualitatively the vinylcyclopropane-to-cyclopentene stereochemical preferences of (1*S*,2*R*)-**1** as it suffers enantiomerization, and then the relative magnitudes of some of the rate constants for the four stereochemically distinct paths may be read from Figure 1. The four isomers in left to right order correspond to reactions from (1*S*,2*R*)-**1** with *sr*, *ai*, *si*, and *ar* stereochemistry, and from the relative intensities of the chiral GC peaks in Figure 1 may be surmised the relative-rate constant inequalities $k_{si} > k_{ar}$ and $k_{sr} > k_{ai}$. One may not conclude from Figure 1 that $k_{ar} > k_{sr}$, in the face of ignorance as to how much of the product mixture was derived from racemic substrate or from *cis*-1-((*E*)-styryl)-2-phenylcyclopropanes.

Qualitatively, these relative rate constant inequalities are similar to those observed for related vinylcyclopropane-to-cyclopentene thermal rearrangements.[2,3] With the analytical capability developed in the present work, the detailed kinetic and stereochemical studies required for a quantiative experimental detemination of reaction stererochemistry for the thermal conversion of one enantiomer of **1** to the four isomers of **2** should be practicable.

Experimental Section

General. Preparative chromatography was done using a Varian Aerograph A90-P3 gas chromatograph, Rainin-component-based HPLC equipment, and a Macherey-Nagel Nucleosil 50-5 preparative column using a Gilson 112 UV detector monitoring at 254 nm and a Model 7924T Chromatotron (Harrison Research) with a 2-mm layer silica gel coated plate.

Chiral GC analyses were made using a Hewlett-Packard 5890 A gas chromatograph equipped with a fused silica Cyclodex B capillary GC column (J & W Scientific, 30 m × 0.26 mm i.d.) or a fused silica Lipodex E capillary GC column (Macherey-Nagel, 50 m × 0.25 mm i.d.), with injection port and detector temperatures maintained at 150 and 300 °C, respectively. Elemental analyses were done by E + R Microanalytical Laboratory, Inc., Corona, NY 11368.

***trans*-1-((*E*)-Styryl)-2-phenylcyclopropane (*rac*-1)** was prepared from *trans*-2-phenylcyclopropanecarboxylic acid through a conventional reduction ($LiAlH_4$), oxidation (PCC, Celite), and Wittig condensation (benzyltriphenylphosphonium chloride, NaHMDS, dry THF) sequence.[1,2,5] The crude product mixture after flash chromatography included some *cis*- and *trans*-stilbenes and the *Z* olefin (~1:4 *Z*:*E* by GC). Pure samples of *rac*-**1** and the *Z* isomer were obtained by preparative GC on a 30.5-cm 20% SE-30 on 60–80 Chromosorb W-AW DMCS-HP column (100 °C, 13 mL/min).

For the *E* olefin (*rac*-**1**):[1,5,6] GC–MS *m/e* 220 (M^+, 26.2), 142 (16.2), 141 (11.7), 129 (M − 91, 100), 128 (39.6), 116 (12.7), 115 (31.4), 92 (37.4), 91 ($C_6H_5CH_2^+$, 29.5), 77 ($C_6H_5^+$, 11.6), 51 (11.8), 39 (11.1); ^1H NMR δ 7.46–7.09 (m, 10H), 6.50 (d, J = 15.75 Hz, 1H), 5.90 (dd, J = 7.07 and 15.78 Hz, 1H), 2.05 (m, 1H), 1.85 (m, 1H), 1.35 (m, 1H), 1.25 (m, 1H); ^{13}C NMR δ 142.11, 137.48, 132.86, 128.51, 128.37, 128.22, 126.76, 125.68, 27.42, 25.72, 17.10. For the *Z* isomer: GC–MS *m/e* 220 (M^+, 19.5), 142 (15.4), 141 (11.6), 129 (M − 91, 100), 128 (43.3), 127 (10.4), 116 (13.8), 115 (33.1), 92 (39.7), 91 ($C_6H_5CH_2^+$, 30.8), 77 ($C_6H_5^+$, 13.3), 65 (11.8), 63 (10.6), 51 (14.7), 39 (13.7); ^1H NMR δ 7.36–7.06 (m, 10H), 6.40 (d, J = 11.48 Hz, 1H), 5.25 (dd, J = 6.24 and 15.72 Hz, 1H), 2.15 (m, 1H), 2.05 (m, 1H), 1.30 (m, 1H), 1.15 (m, 1H); ^{13}C NMR δ 134.75, 128.62, 128.34, 128.17, 126.49, 125.74, 125.66, 26.17, 23.79, 18.15.

(1*S*,2*R*)-*trans*-1-((*E*)-Styryl)-2-phenylcyclopropane ((1*S*,2*R*)-1) was prepared by the same three-step sequence, starting from a crude sample of (1*R*,2*R*)-**3**[10] prepared by C. G. Carter. A 5-mg sample of (1*S*,2*R*)-**1** (97.8% pure by GC) in 2 mL of dry benzene was oxidized with $KMnO_4$ (99.8 mg, 0.63 mmol, 31.6 equiv) and 18-crown-6 (Aldrich, 99%, 128.9 mg, 0.49 mmol, 24.5 equiv).[25] After 20 h at rt, 20 mL of 5% KOH was added and the mixture was filtered and acidified with 10% H_2SO_4. The acidified aqueous layer was extracted with two 25-mL portions of ether, and the combined organic layers were dried, filtered, and concentrated by rotary evaporation. Subsequent treatment with ethereal CH_2N_2 gave methyl (1*R*,2*R*)-*trans*-2-phenylcyclopropanecarboxylate. Chiral GC analysis using a Lipodex E column at 90 °C showed complete resolution of the enantiomers of the methyl ester; the intensity ratio observed (93.6:6.4) corresponds to 87% ee for the (1*S*,2*R*)-**1**.[2]

***cis*- and *trans*-3,4-diphenylcyclopentenes (*rac*-2-*c* and *rac*-2-*t*)** were prepared following the method of Shoppee and Henderson[11] from dibenzylideneacetone. Kugelrohr distillation under reduced pressure (0.1 mm) of the crude product mixture at a maximum pot temperature of 160 °C gave a yellow viscous distillate, from which pure samples of *rac*-**2**-*c* and *rac*-**2**-*t* were obtained by preparative GC on a 1-m 20% Carbowax 20 M on 60–80 Chromosorb P-NAW column (175 °C, 11 mL/min).

The cis isomer (*rac*-**2**-*c*) was obtained as white needles: GC–MS *m/e* 220 (M^+, 45.4%), 142 (19.9), 129 (M − CH_2Ph, 100.0), 128 (40.9), 116 (14.7), 115 (6.7), 92 (38.2), 91 ($C_6H_5CH_2^+$, 33.1), 77 ($C_6H_5^+$, 14.6), 51 (16.1), 39 (15.5); ^1H NMR δ 7.06–6.80 (m, 10H), 6.18 (m, 1H), 5.93 (m, 1H), 4.15 (d, J = 8.40 Hz, 1H), 3.85 (q, J = 17.18 Hz, 1H), 2.75 (d, J = 7.47 Hz, 2H); ^{13}C NMR δ 133.39, 132.13, 128.70, 128.49, 127.57, 127.39, 125.89, 125.60, 56.14, 50.07, 37.41.

The trans isomer (*rac*-**2**-*t*) was obtained as a clear colorless liquid: GC–MS *m/e* 220 (M^+, 56.6), 142 (20.8), 141 (13.9), 129 (100.0), 128 (38.8), 116 (13.6), 115 (34.8), 92 (31.5), 91 ($C_6H_5CH_2^+$, 29.3), 77 ($C_6H_5^+$, 11.9), 51 (12.9), 39 (11.5); ^1H NMR δ 7.30–7.08 (m, 10H), 6.00 (m, 1H), 5.82 (m, 1H), 3.95 (m, 1H), 3.75 (q, J = 11.63 Hz, 1H), 2.95 (m, 1H), 2.60 (m, 1H); ^{13}C NMR δ 145.78, 145.07, 133.44, 130.80, 128.40, 127.29, 126.23, 126.08, 60.45, 54.49, 41.69.

Chiral GC analysis of *rac*-**2**-*c* and *rac*-**2**-*t* (Cyclodex B, 165 °C isothermal) showed base-line resolution of the enantiomers of both compounds; enantiomers of **2**-*c* elute before those of **2**-*t*.

***trans*-2-Phenylcyclopentanol (8)** was made through the addition of phenylmagnesium bromide to cyclopentene oxide. A sample purified by preparative GC on a 1-m 15% SE-30 on 60–80 Chromosorb W column (100 °C, 12 mL/min) gave a clear colorless liquid: GC–MS *m/e* 162 (M^+, 54.8), 144 (M − 18, 21.9), 143 (12.9), 133 (17.5), 129 (51.2), 120 (13.4), 118 (38.0), 117 (55.6), 116 (10.4), 115 (25.8), 105 (28.1), 104 (29.7), 103 (19.0), 92 (50.3), 91 ($C_6H_5CH_2^+$, 100), 79 ($C_6H_7^+$, 10.8), 78 ($C_6H_6^+$, 25.9), 77 ($C_6H_5^+$, 23.6), 71 (10.8), 65 (16.6), 57 (13.8), 51 (17.8), 43 (10.3), 39 (19.8); ^1H NMR δ 7.35–7.20 (m, 5H), 4.15 (q, J = 14.26 Hz, 1H), 2.90 (q, J = 16.50 Hz, 1H), 2.20–

(25) Sam, D. J.; Simmons, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 4024–4025.

2.10 (m, 2H), 1.90–1.65 (m, 4H), 1.60 (br s, OH); ^{13}C NMR δ 148.46, 128.54, 127.37, 126.40, 80.43, 54.44, 33.94, 31.82, 21.73.

2-Phenylcyclopentanone (9)[15] was made through the oxidation of **8** with PCC. Preparative GC purification on a 1-m 15% SE-30 on 60–80 Chromosorb W column (100 °C, 12 mL/min) gave ketone **9** as a clear colorless liquid: GC–MS *m/e* 161 (M + 1, 4.9), 160 (M^+, 39.0), 117 (9.5), 105 (10.4), 104 (100), 91 ($C_6H_5CH_2^+$, 11.6), 78 ($C_6H_6^+$, 16.3), 77 ($C_6H_5^+$, 10.3);[15] ^{1}H NMR δ 7.36–7.18 (m, 5H), 3.33 (t, J = 9.56 Hz, 1H), 2.50 (m, 2H), 2.45–1.90 (m, 4H); ^{13}C NMR δ 128.57, 128.11, 126.87, 55.30, 38.43, 31.74, 20.85 (compare ref 26).

***cis*-2-Phenylcyclopentanol (*rac*-10).** Ketone **9** (2.68 g, 16.8 mmol, 1.0 equiv) in 6 mL of dry THF was placed in a three-necked flask equipped with a reflux condenser and kept under nitrogen. To this magnetically stirred solution cooled to −78 °C was added dropwise L-Selectride (1.0 M in THF, 36.0 mL, 36.0 mmol, 2.1 equiv). After 6 h at −78 °C, the reaction flask was warmed to rt and stirred overnight. The flask was brought to 0 °C; 6.0 mL of H_2O, 21 mL of EtOH, 13 mL of 6 M NaOH, and 20 mL of 30% H_2O_2 were added successively. A little pentane was added, and anhydrous K_2CO_3 was added to saturate the aqueous phase. The two layers were filtered to remove particulates and then separated. The aqueous layer was extracted with four 25-mL portions of 1:1 ether–THF, and the combined organic material was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. Purification using a Chromatotron (10% EtOAc–hexanes) afforded *rac*-**10** as a clear light yellow oily liquid (1.75 g, 64% yield). Preparative GC purification on a 1-m 15% SE-30 on 60–80 Chromosorb W column (100 °C, 12 mL/min) gave a clear colorless liquid: GC–MS *m/e* 162 (M^+, 57.6), 144 (M − 18, 22.7), 143 (11.6), 133 (17.3), 129 (50.3), 120 (12.9), 118 (38.6), 117 (53.2), 116 (10.3), 115 (26.2), 105 (27.7), 104 (28.2), 103 (19.2), 92 (46.9), 91 ($C_6H_5CH_2^+$, 100), 79 ($C_6H_7^+$, 9.9), 78 ($C_6H_6^+$, 25.2), 77 ($C_6H_5^+$, 22.4), 71 (9.3), 65 (16.9), 63 (9.7), 57 (14.7), 51 (18.0), 43 (11.0), 41 (9.3), 39 (22.1); ^{1}H NMR δ 7.37–7.24 (m, 5H), 4.30 (m, 1H), 3.06 (m, 1H), 2.18–1.70 (m, 6H), 1.20 (br s, OH); ^{13}C NMR δ 139.83, 128.58, 128.55, 126.66, 75.72, 51.96, 33.73, 27.32, 22.38.

Chiral GC analysis on a Lipodex E column (90 °C isothermal) showed baseline resolution of the enantiomers of **10** (retention times ~240 and ~250 min).

***cis*-2-Phenylcyclopentyl (*R*)-*O*-Acetylmandelate Esters (11a).** To a solution of *rac*-**10** (1.75 g, 10.78 mmol, 1.0 equiv), 4-(dimethylaminopyridine) (DMAP, Aldrich, 99%, 133.9 mg, 1.09 mmol, 0.10 equiv), and (*R*)-(−)-*O*-acetylmandelic acid (Aldrich, 99%, 2.13 g, 10.97 mmol, 1.02 equiv) in 25.5 mL of dry CH_2Cl_2 at 0 °C was added dropwise over a 10-min period 1,3-dicyclohexylcarbodiimide (DCC, Aldrich, 99%, 2.26 g, 10.95 mmol, 1.02 equiv) in 10.5 mL of dry CH_2Cl_2. Dicyclohexylurea precipitated from the solution even before the addition was complete. Once the DCC was completely added, the ice–H_2O bath was removed and the reaction mixture was stirred for 33 h at rt. The precipitated urea was removed by filtration, and the filtrate was washed with 75 mL of 0.5 N HCl, 75 mL of 2 N Na_2CO_3, and finally 75 mL of brine. The organic layer was separated, dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. Purification using HPLC (10-15% EtOAc-hexanes, 6.0 mL/min) gave a clear colorless oil (2.75 g, 76% yield) but it did not result in resolution of the diastereomers. Purification using a Chromatotron (10% EtOAc–hexanes), after several recyclings, resulted in partial resolution of the diastereomers. The more mobile isomer on the Chromatotron was the later eluting compound by capillary GC (1*S*,2*S*)-**11a**; GC–MS *m/e* 177 (13.5) 149 (64.7), 146 (9.3), 145 (87.1), 144 (26.8), 117 (18.1), 115 (12.6), 107 (100), 105 (10.4), 91 ($C_6H_5CH_2^+$, 91.7), 79 ($C_6H_7^+$, 18.1), 77 ($C_6H_5^+$, 16.3), 67 (16.0), 43 (95.8); $[\alpha]_D$ −80.2° (*c* 1.83, $CHCl_3$); 53.0% de by GC. The less mobile isomer on silica gel was the earlier eluting compound by capillary GC, (1*R*,2*R*)-**11a**: GC–MS *m/e* 149 (60.4), 146 (10.9), 145 (91.7), 144 (24.8), 117 (18.4), 115 (13.4), 107 (100), 105 (10.6), 91 ($C_6H_5CH_2^+$, 94.4), 79 ($C_6H_7^+$, 18.5), 77 ($C_6H_5^+$, 18.3), 67 (17.5), 43 (98.1); ^{1}H NMR (both diastereomers) δ 7.32–7.00 (m, 10H), 5.73 (s, 1H), 5.40 (t, J = 4.56 Hz, 1H), 3.10 (m, 1H), 2.20–1.70 (m, 6H), 2.10 (s, 3H); ^{13}C NMR (both diastereomers) δ 170.22, 168.20, 138.75, 133.48, 128.91, 128.66, 128.52, 128.38, 128.10, 128.06, 127.89, 127.56, 127.13, 126.08, 49.50, 49.46, 32.65, 28.63, 28.53, 22.07, 20.60. Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.54; H 6.55. Found: C, 74.68; H 6.73.

***cis*-2-Phenylcyclopentyl (*R*)-Mandelate Esters (11b).** A 1:1 mixture of (*R*)-*O*-acetylmandelate esters **11a** (2.75 g, 8.14 mmol) was dissolved in 187 mL of MeOH and placed in a single-necked flask. A solution of $NaSH{\cdot}xH_2O$ (4.57 g dissolved in 131 mL of 3:2 MeOH–H_2O and acidified to pH 8 with 10% HCl) was added to the methanolic solution. The dark yellow solution was heated to 55 °C in an oil bath for 9 h and then cooled to rt. The light yellow solution had some white solid formed on the bottom of the flask. More white solid separated from the solution after 313 mL of water was added to the flask. The aqueous solution was extracted with three 313-mL portions of ether, saturated with NaCl, and then extracted again with two 313-mL portions of ether. The organic material was combined, dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation until a white solid remained. The solid was dissolved in ether (470 mL) and washed with five 313-mL portions of H_2O and once with brine. The organic material was dried, filtered, and concentrated by rotary evaporation to give 2.52 g of an oily liquid and some light yellow solid. Analysis of the product mixture by TLC (precoated silica gel 60 F-254 plates (0.25 mm), developed using 9:1 hexanes–ethyl acetate, visualized with UV light, and stained with a solution of anisaldehyde) and by capillary GC indicated the presence of some unreacted starting material. Purification of the mixture was accomplished using a Chromatotron (10% EtOAc–hexanes) to give 0.28 g of an unknown, very mobile compound, 1.03 g of unreacted starting materials (**11a**), 0.34 g of a mixed fraction (containing starting materials and product), and 0.87 g of a fine white solid; recrystallization of this solid from 2:1 hexanes–EtOAc gave a first crop of (1*R*,2*R*)-**11b** as white rectangular plates (133 mg, 29% yield): mp 96–99 °C; $[\alpha]_D$ −99.2° (*c* 0.5, 95% EtOH). A second crop of (1*R*,2*R*)-**11b** was obtained (30.8 mg, 4% yield): ^{1}H NMR δ 7.27–6.87 (m, 10H), 5.44 (t, J = 4.40 Hz, 1H), 4.98 (d, J = 5.52 Hz, 1H), 3.28 (d, J = 5.71 Hz, OH), 3.10 (m, 1H), 2.20–1.71 (m, 6H); ^{13}C NMR δ 172.90, 138.37, 137.90, 128.33, 128.12, 128.02, 127.97, 126.28, 126.22, 80.65, 72.90, 49.81, 32.70, 28.43, 21.98.

The mother liquor from the second crop, after removal of all the solvents, gave a slightly yellow mass of solid (0.667 g) containing both (*R*)-mandelate diastereomers but enriched in (1*S*,2*S*)-**11b**: $[\alpha]_D$ −24.3° (*c* 0.77, 95% EtOH), $[\alpha]_D$ −33.2° (*c* 6.45, $CHCl_3$); ^{1}H NMR δ 7.33–6.79 (m, 20H), 5.37–5.28 (dt, J = 4.38 and 15.13 Hz, 2H), 4.89 (s, 1H), 4.74 (s, 1H), 3.29 (br s, OH), 3.07–2.95 (m, 2H), 2.09–1.47 (m, 12H); ^{13}C NMR δ 172.81, 139.04, 138.33, 137.86, 128.38, 128.30, 128.25, 128.13, 128.07, 127.97, 127.90, 127.87, 126.57, 126.31, 126.22, 126.14, 80.53, 80.28, 72.84, 72.67, 49.72, 49.69, 32.63, 32.26, 28.68, 28.37, 21.98, 21.92. Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H 6.80. Found: C, 76.96; H 6.94.

(1*R*,2*R*)-(−)-*cis*-2-Phenylcyclopentanol ((1*R*,2*R*)-10). The mandelate ester (1*R*,2*R*)-**11b** of mp 96–99 °C (133 mg, 0.41 mmol, 1.0 equiv) in 4.0 mL of MeOH was placed in a single-necked flask. To this solution was added anhydrous K_2CO_3 (127.4 mg, 0.92 mmol, 2.3 equiv) and enough water to effect nearly complete dissolution of the K_2CO_3. After being stirred for 24 h at rt, the flask was cooled to 0 °C and acidified to pH 3 with 10% HCl. The resulting acidified aqueous layer was extracted with three 5-mL portions of ether. The organic material was combined, washed successively with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated to give a slightly cloudy oily liquid. Preparative GC purification on a 1-m 15% SE-30 on 60–80 Chromosorb W column (100 °C, 12 mL/min) gave pure material (40.2 mg, 61% yield) as a clear colorless liquid: $[\alpha]_D$ −73.6° (*c* 0.38, $CHCl_3$) (lit.[18] $[\alpha]_D$ −90.4° (no solvent cited)).

(26) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936–945.

Analysis by chiral GC indicated the presence of only one peak corresponding to the later eluting enantiomer (~250 min); the (1*R*,2*R*)-(−) alcohol is thus of 100% ee.

(1*S*,2*S*)-(+)-*cis*-2-Phenylcyclopentanol ((1*S*,2*S*)-10). A sample of the mother liquor from the second crop enriched in the mandelate diastereomer (1*S*,2*S*)-**11b** (306 mg, 1.03 mmol, 1.0 equiv) was hydrolyzed to the corresponding alcohol (1*S*,2*S*)-**10** (slightly cloudy light yellow oil, 150.3 mg, 90% yield). Analysis by chiral GC showed two peaks: the early eluting (1*S*,2*S*) enantiomer (~240 min) followed by the later eluting (1*R*,2*R*) enantiomer (~250 min) with an intensity ratio of 64.3:35.7 (29% ee).

(1*S*,2*S*)-*cis*-2-Phenylcyclopentyl Tosylate ((1*S*,2*S*)-12). Alcohol (1*S*,2*S*)-**10** (29% ee, 150 mg, 0.93 mmol, 1.0 equiv) in 1.5 mL of dry pyridine was treated with *p*-TsCl to give, after workup, a white solid (248 mg, 85% yield) with mp 91.5−94.5 °C (lit.[14b] mp 97−98 °C for racemic material). For a sample of the racemic tosylate: GC−MS *m/e* 145 (9.2), 144 (86.4), 143 (73.4), 130 (9.9), 129 (100), 128 (63.8), 127 (14.2), 116 (9.3), 115 (42.8), 91 ($C_6H_5CH_2^+$, 10.8), 89 (9.5), 77 ($C_6H_5^+$, 10.7), 66 (15.6), 65 (10.3), 63 (11.7), 51 (13.5), 39 (16.1); ^{1}H NMR δ 7.31−7.04 (m, 9H), 4.90 (m, 1H), 3.04 (m, 1H), 2.38 (s, 3H), 2.28−2.02 (m, 6H); ^{13}C NMR δ 143.74, 138.02, 133.60, 129.34, 128.56, 128.02, 127.46, 126.49, 86.95, 50.67, 33.30, 27.98, 21.80, 21.53.

(1*R*,2*R*)-*trans*-1,2-Diphenylcyclopentane ((1*R*,2*R*)-6). In a flame-dried reaction vessel were combined copper cyanide (Aldrich, 99%, 149.9 mg, 1.67 mmol, 5.0 equiv) and 2 mL of dry THF, and the mixture was cooled to −78 °C. After 5 min at −78 °C, phenyllithium (PhLi, Aldrich, 1.8 M in cyclohexane−THF, 1.9 mL, 3.4 mmol, 10 equiv) was added dropwise via syringe. Once the addition was complete, stirring was continued for another 5 min. (1*S*,2*S*)-*cis*-2-Phenylcyclopentyl tosylate ((1*S*,2*S*)-**12**) (106 mg, 0.34 mmol, 1.0 equiv) in 0.8 mL of dry THF was added dropwise to the dark reddish brown mixture. The reaction flask was gradually warmed to rt, and the reaction was allowed to proceed at rt for 24 h. Saturated aqueous ammonium chloride (5 mL) was added dropwise to the flask once it was cooled to 0 °C. The layers were separated, and the organic layer was repeatedly washed with saturated aqueous NH_4Cl and washed once with brine. The organic material was dried over $MgSO_4$ and filtered. Capillary GC analysis of the crude dilute product mixture indicated that 1.16% of the mixture was *trans*-1,2-diphenylcyclopentane (**6**). Qualitative TLC analysis showed that unreacted (1*S*,2*S*)-**12** was still present. Preparative GC purification on a 1-m 17% Carbowax 20 M on 60−80 Chromosorb P-NAW column (175 °C, 22 mL/min) gave the desired saturated compound (1*R*,2*R*)-**6** (97% pure by GC). The chemical identity of this compound was confirmed by its identical capillary GC retention times on two columns with authentic *rac*-**6**. Chiral GC analysis of (1*R*,2*R*)-**6** from tosylate (1*S*,2*S*)-**12** revealed the later eluting isomer (~31.2 min) was predominant; thus, the later eluting peak corresponded to the enantiomer of (1*R*,2*R*) absolute stereochemistry. The intensity ratio of these two peaks was 35.2:64.8 corresponding to 30% ee (Figure 2).

Thermal Reactions of 1-((*E*)-Styryl)-2-phenylcyclopropanes *rac*-1 and (1*S*,2*R*)-1. Thermal isomerizations of *rac*-**1** and (1*S*,2*R*)-**1** were carried out in kinetic bulbs previously soaked in concentrated HCl overnight followed by NH_4OH/EDTA for at least 2 d. Each bulb was washed copiously with water after each soaking. The bulbs were then dried in a 140 °C oven for at least 2 d. Samples from 10 to 150 mg in a little cyclohexane and a crystal of hydroquinone in such a prepared bulb were subjected to three freeze−pump−thaw cycles prior to sealing. Thermal isomerizations were conducted in an oil bath maintained at 160.2 ± 0.5 °C. Reaction mixtures were analyzed by capillary GC and by chiral GC; the chiral GC separation on the four 3,4-diphenylcyclopentenes is exemplified in Figure 1.

The thermal reaction mixture from heating (1*S*,2*R*)-**1** (~150 mg, 83% trans isomer, 82% ee; 10% of *trans*-1-(*Z*-styryl)-2-phenylcyclopropane, which does not give cyclopentene products under the reaction conditions; 7.0% of racemic *cis*-1-((*E*)-styryl)-2-phenyl-cyclopropane) and 280 μL of cyclohexane in a 100-mL bulb for 3 h at 160 °C contained some 4% of the 3,4-diphenylcyclopentenes; chiral GC analysis revealed 18% ee for **2**-*c* and 20% ee for **2**-*t*. The solution of reaction products was concentrated by rotary evaporation and then purified by preparative GC. Preparative GC purified **2**-*t* (1.2 mg, 0.005 mmol) in 700 μL of MeOH was subjected to a diimide reduction using a huge excess of diimide from potassium azodicarboxylate (209.4 mg, 1.08 mmol, 215.6 equiv) followed by the dropwise addition of glacial acetic acid (HOAc, 120 μL) over a 2-h period. During the course of the reaction, additional amounts of the diimide precursor were added to the reaction mixture so that the yellow color of the suspension was maintained. After a total of 16 h of stirring at rt, analysis of an aliquot by capillary GC showed that the reduction had only gone to 88% completion. More of the diimide precursor (0.2143 g, 1.10 mmol) and glacial HOAc (120 μL over a 2-h period) were then added. After another 2 d at rt, water and pentane were added to the slightly yellow suspension. The aqueous layer was extracted with ether, and the combined organic material was analyzed by capillary GC which indicated that the reduction had now gone to 97% completion. The chemical identity of the new product formed was confirmed by GC comparisons with an authentic sample of *rac*-**6**.

Chiral GC analysis of the diimide reduction product showed the presence of two peaks: the early eluting peak (at ~31.0 min) was the predominant enantiomer, and the later eluting peak (at ~31.6 min was the minor isomer (Figure 2). The intensity ratio of these two peaks was 58.8:41.2 (18% ee). Chiral GC comparisons with an authentic sample of (1*R*,2*R*)-**6** (Figure 2) revealed that (1*S*,2*S*)-**6** was predominant in the diimide product (see below).

***trans*-2,3-Diphenylcyclopentanone (*rac*-14).** In an oven-dried single-necked flask, kept under nitrogen, was dissolved *m*-chloroperoxybenzoic acid (Aldrich, 50−60%, 188.6 mg) in 19 mL of dry CH_2Cl_2. To this clear colorless solution was added a mixture of *rac*-**2**-*c* and *rac*-**2**-*t* (100 μL). After being stirred for 13 h at rt, the product mixture was washed with two 10-mL portions of saturated aqueous $NaHCO_3$, two 10-mL portions of saturated aqueous Na_2SO_3, and finally with two 10-mL portions of H_2O. The separated organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to give 77.2 mg of an orange oil (74% epoxides by GC, 69% yield). Analysis by capillary GC indicated that there were three new products formed (retention times 11.98 min, 12.24 min, and 13.14 min) on a HP Ultra 2 (cross-linked 5% phenyl methyl silicone 25 m × 0.2 mm × 0.3 μm film thickness) capillary column at 175 °C. GC−MS analysis of the product mixture showed that all three products had a molecular ion corresponding to the desired epoxides, *m/e* 236.

To the crude mixture of epoxides dissolved in 1.5 mL of anhydrous ether kept at 0 °C was added $LiAlH_4$ (Aldrich, 95%, 13.1 mg) in small portions. Once the addition was complete, the cold bath was removed and stirring was continued for another 4 h at rt. The slurry was then treated sequentially with 20 μL of H_2O, 20 μL of 15% NaOH, and 60 μL of H_2O. The mixture was stirred at rt for another 30 min, and then a white precipitate was collected and washed copiously with ether. Preparative GC purification on a 1-m 15% SE-30 on 60−80 Chromosorb W column (175 °C, 9 mL/min) gave a mixture of unresolved alcohols: IR 3406 cm^{-1}, 3027, 2940, 1597, 1490, 1451, 1024; GC−MS *m/e* 238 (M^+, 30.3).

The mixture of alcohols, dissolved in a minimal volume of dry CH_2Cl_2, was added to a slurry of PCC (Aldrich, 98%, 295 mg) and Celite (298 mg) in 5 mL of dry CH_2Cl_2. After 7.5 h of stirring at rt, the slurry was filtered through Florisil and the Florisil was washed repeatedly with ether. The ethereal filtrate was dried, filtered, and concentrated by rotary evaporation. Capillary GC analysis indicated the presence of two new products in a 1:9 ratio. Preparative GC purification on a 1-m 15% SE-30 on 60−80 Chromosorb W column (175 °C, 9 mL/min) of the major product gave *rac*-**14**: GC−MS *m/e* 237 (M + 1, 17.3), 236 (M^+, 100), 181 (15.3), 180 (17.3), 179 (33.1), 178 (28.9), 165 (19.2), 145 (19.8), 118 (51.6), 117 (18.8), 115 (16.9), 105 (38.2), 104 (14.1), 91 (32.5), 90 (13.4), 89 (14.0), 77 (10.3), 39 (26.7); ^{1}H NMR δ 7.35−7.00 (m, 10H), 3.55−3.45 (m, 2H), 2.75−2.65 (dd, *J* = 17.08, 8.28 Hz, 1H), 2.55−2.45 (m, 2H), 2.20−2.05 (m, 1H) (compare ref 21b); ^{13}C NMR δ

141.56, 137.00, 128.60, 128.58, 128.51, 127.02, 126.99, 126.85, 62.76, 50.42, 38.80, 29.52. Chiral GC analysis on a Lipodex E column (165 °C) showed baseline resolution of the enantiomers of *rac*-**14** (retention times ~159 min and ~165 min).

Correlation of Chiral GC Retention Behavior with Absolute Stereochemistry for *cis*-3,4-Diphenylcyclopentene Enantiomers. A sample of (1*S*,2*R*)-**1** (300 mg, 99.0% trans of 80% ee; 0.2% of *cis*-1-((*E*)-styryl)-2-phenylcyclopropane of 0.5% ee; 0.8% *trans*-1-((*Z*)-styryl)-2-phenylcyclopropane) was dissolved in 450 μL of cyclohexane, and ~ 200 μL aliquots were placed into four 100-mL bulbs. Each bulb was heated for 3 h at 160 °C, cooled, and opened. The products were transferred and diluted with cyclohexane, combined, and analyzed by capillary and chiral GC. The extent of conversion to cyclopentenes was determined to be about 5% (**2**-*c*, 20% ee, and **2**-*t*, 22% ee). A prolonged concentration of the cyclohexane solution by simple distillation gave a higher yield of cyclopentenes (25%) with concomitant diminution of ee values. Preparative HPLC purification (hexanes, 2.0 mL/min) gave **2**-*c* and **2**-*t* completely free of recovered 1-styryl-2-phenylcyclopropanes. Subsequent preparative GC purification on a 1-m 17% Carbowax 20 M on 60–80 Chromosorb P-NAW column (175 °C, 22 mL/min) gave pure samples of **2**-*c* (8% ee) and **2**-*t* (9% ee). Each cyclopentene isomer was then subjected separately to the reaction sequence leading to ketone **14**.

Chiral GC analysis on a Lipodex E column at 165 °C of ketone (2*S*,3*S*)-**14** obtained from the *trans*-cyclopentene thermolysis product (3*S*,4*S*)-**2**-*t* indicated that the later eluting peak (~164 min) was predominant; thus, the later eluting enantiomer was of (2*S*,3*S*) absolute stereochemistry. The intensity ratio of the two peaks were 45.4:54.6 corresponding to 9% ee.

Chiral GC analysis of ketone **14** obtained from the cis thermolysis product **2**-*c* indicated that the early eluting peak (~159 min) corresponding to the (2*R*,3*R*) enantiomer was predominant; thus the major cis cyclopentene enantiomer formed through the vinylcyclopropane rearrangement of (1*S*,2*R*)-**1** is (3*S*,4*R*)-**2**-*c*. The intensity ratio of the two peaks was 55.2:44.8 corresponding to 10% ee.

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