Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.64; H, 6.11.

1,4-Dimethylhexahelicene (10). The mixture of the cis–trans olefins **9** (500 mg) was dissolved in benzene (350 mL) containing iodine (4 mg), and the solution was irradiated with a medium-pressure mercury lamp (Toshiba SHL-100UV) in an atmosphere of nitrogen for 4 h. After the solvent was removed, the residue was chromatographed over alumina. Benzene–hexane eluates were collected, and removal of the solvent left a yellow solid, which was recrystallized from ethyl acetate to give **10**: 320 mg (64%); yellow prisms; mp 252–253 °C; IR (KBr) 3040, 3020, 2960, 2930, 2920, 2880, 1600, 1476, 1440, 1430, 820, 812, 802, 743 cm^{-1}; NMR ($CDCl_3$) δ 0.54 (s, CH_3, 3 H), 2.42 (s, CH_3, 3 H), 6.00–8.10 (m, Ar H, 14 H); UV (hexane) λ_{max} 230 nm (log ϵ 4.63), 252 (4.59), 270 (4.53), 297 (4.30), 318 (4.29), 330 (sh, 4.23), 354 (sh, 3.94); mass spectrum, m/e 356 (M^+).

Anal. Calcd for $C_{28}H_{20}$: C, 94.08; H, 5.80. Found: C, 94.24; H, 5.76.

Optical Resolution of 1,4-Dimethylhexahelicene (10). A finely ground powder of chiral poly(triphenylmethacrylate)[12] (2.0 g) was swollen with hexane (5 mL) and was packed in a glass tube (12 mm i.d.) to give a 5-cm column. A solution of (±)-dimethylhexahelicene (**10**, 0.4 g) in hexane was introduced into the column, and eluted with hexane to give the 10-mL aliquots (Table I).

The procedure was repeated to process a total of 6.4 g of the 1,4-dimethylhexahelicene (**10**), and the combined first and second fractions gave the (−) enantiomer **10**: 2.3 g; mp 241–243 °C; $[\alpha]^{28}_D$ −404°, $[\alpha]^{28}_{577}$ −432° ($CHCl_3$).

Anal. Calcd for $C_{28}H_{20}$: C, 94.08; H, 5.80. Found: C, 94.29; H, 5.69.

1-Methyl-4-(bromomethyl)hexahelicene (12). A stirred and refluxed solution of (−)-**10** (2.3 g, 6.5 mmol), NBS (1.1 g, 6.5 mmol), and benzoyl peroxide (4 mg) in CCl_4 (50 mL) was irradiated with a tungsten lamp (100 W) for 4 h. The mixture freed of the precipitated succinimide was washed with 3% $NaHCO_3$ and water and then was dried ($MgSO_4$). After removal of the solvent, the residue was column chromatographed over SiO_2 gel (20 g), and elution with benzene gave the bromide **12** as a yellow viscous oil which was converted into the double-layerd helicene **6** without further purification: NMR ($CDCl_3$) δ 4.20 (q, J_{ab} = 12 Hz, CH_2); mass spectrum m/e 435 (M^+).

(−)-Quaternary Ammonium Bromide (13). To a chilled solution of the crude bromide **12** (3.0 g) in absolute ether (20 mL) was added trimethylamine (15 mL), and the mixture was stirred at room temperature for 13 h. The precipitate was collected and washed with ether to give a white solid: 1.2 g (38% yield from the dimethyl derivative **10**); $[\alpha]^{28}_D$ −465° ($CHCl_3$).

(−)-[2.2]Paracyclophanohexahelicene (6). A mixture of (−)-**13** (1.1 g, 2.22 mmol) and *p*-xylyltrimethylammonium bromide (**14**;[14] 1.4 g, 5.73 mmol) was dissolved in water (300 mL), and freshly prepared silver oxide (from 5 g of silver nitrate) was added. After the mixture was stirred for 24 h at room temperature, the precipitate was removed by filtration, and the filtrate was concentrated to 100 mL under vacuum. The concentrated hydroxide solution was mixed with toluene (100 mL) containing phenothiazine (20 mg) and heated to reflux. After removal of water by azeotropic distillation, the reaction mixture was refluxed for 4 h. The mixture freed of an isoluble polymer by filtration was concentrated in vacuo, and the residue was chromatographed over SiO_2 gel. While elution with hexane gave [2.2]paracyclophane (110 mg), further elution with hexane–benzene (5:1) produced crude (−)-**6** which was purified by preparative TLC (SiO_2 gel). Elution of hexane yielded (−)-**6** (40 mg, 4%), which was recrystallized from ethyl acetate: mp 236–237 °C; yellow prisms; $[\alpha]^{28}_D$ −584°, $[\alpha]^{28}_{577}$ −662° ($CHCl_3$); IR (KBr) 3060, 3040, 3010, 2950, 1600, 1580, 840, 812, 800, 790, 763, 739, 712 cm^{-1}; NMR ($CDCl_3$) δ 1.42–2.07 (m, 4 H), 2.76–3.17 (m, 3 H), 3.62–4.00 (m, 1 H), 4.60 (dd, J = 8, 2 Hz, 1 H), 5.62 (dd, J = 8, 2 Hz, 1 H), 5.82 (d, J = 8 Hz, 1 H), 6.15 (t, J = 8 Hz, 1 H), 6.22–6.46 (m, 3 H), 6.80–7.08 (m, 2 H), 7.62 (d, J = 8 Hz, 1 H), 7.77–8.12 (m, 8 H); UV (hexane) λ_{max} 233 nm (sh, log ϵ 4.62), 263 (4.70), 272 (sh, 4.64), 310 (4.28), 325 (4.32), 340 (4.29), 367 (sh, 3.92); CD (hexane) 10^{-5} [Θ] (λ, nm) +0.61 (234), +1.35 (263), +0.98 (273), −1.25 (340), −0.51 (367); mass spectrum, m/e 458 (M^+).

Anal. Calcd for $C_{36}H_{26}$: C, 94.27; H, 5.65. Found: C, 94.28; H, 5.72.

Registry No. (−)-**6**, 37044-40-9; **7**, 35160-98-6; **8**, 5779-94-2; *cis*-**9**, 76756-20-2; *trans*-**9**, 76756-21-3; (±)-**10**, 76756-22-4; (−)-**10**, 76820-61-6; (+)-**11**, 17486-32-7; **12**, 76756-23-5; (−)-**13**, 76756-24-6; **14**, 16814-21-4.

Reaction of $HCo(CO)_4$ with Methyl 2,3-Diphenyl-2-cyclopropene-1-carboxylate: Synthesis of Methyl *t*,*t*-2,3-Diphenyl-*c*-2-formylcyclopropane-*r*-1-carboxylate

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Reaction of $HCo(CO)_4$ with the diphenylcyclopropene **1** leads to the three possible hydrogenated cyclopropanes but in addition a single hydroformylation product is formed. This aldehyde was synthesized by an unambiguous procedure; it is compound **2**, formed by cis addition of $HCo(CO)_4$ to the more hindered face of the cyclopropene.

Introduction

Although most highly conjugated olefins react with $HCo(CO)_4$ under stoichiometric conditions to give hydrogenated products, we have found that methyl 2,3-diphenyl-2-cyclopropene-1-carboxylate, **1**, undergoes stoichiometric hydroformylation to give an 18–22% yield of a single pure aldehyde with the balance of the material consisting of hydrogenated isomers. The structure of the aldehyde could be one of the four possible aldehydes **2–5**. Compounds **2** and **3** would arise from cis addition to either face of **1**, while **4** and **5** would result from trans addition. Because of the paucity of information on the stereochemistry of the stoichiometric hydroformylation (e.g., is the reaction a concerted 1,2-addition, or a stepwise radical or cationic reaction),[1] it was considered important to determine which of the four possible aldehydes is formed in the above reaction.

Results and Discussion

The aldehyde isolated from the stoichiometric hydroformylation of **1** is a nicely crystalline colorless compound, mp 144.5–145.0 °C. Treatment of it with $LiAlH_4$ gives a

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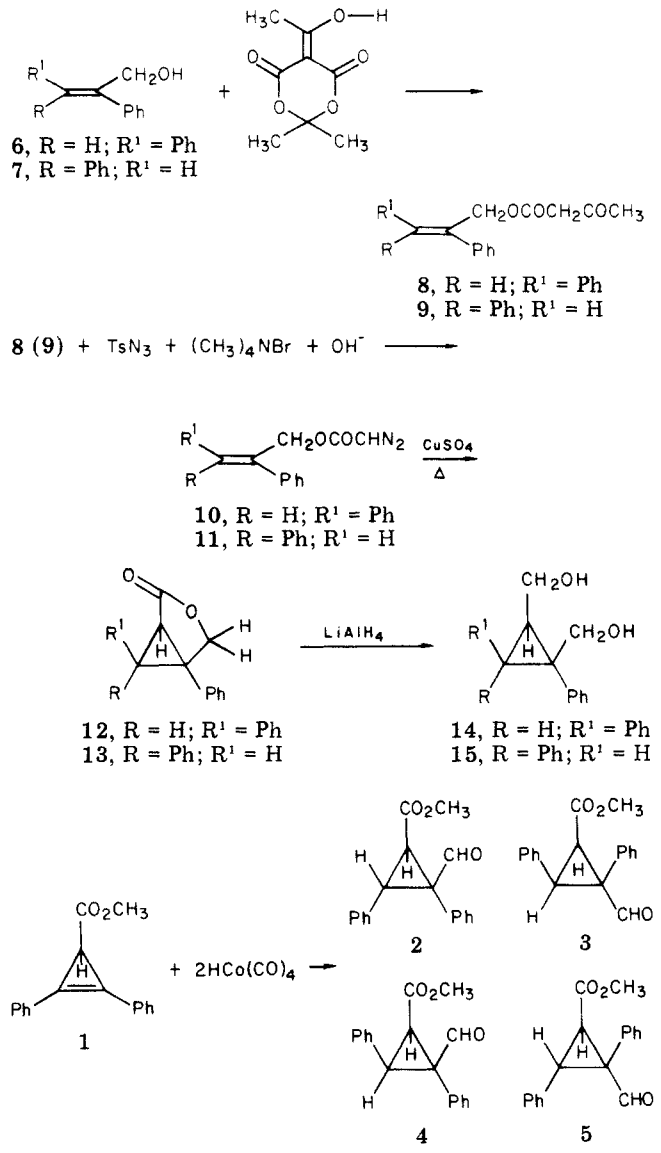
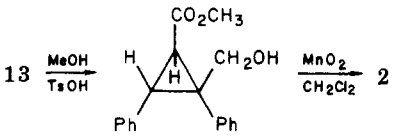
Scheme I



crystalline diol which on treatment with acetone dimethyl ketal in the presence of a small quantity of *p*-toluenesulfonic acid gives the expected ketal exchange, resulting in the isolation of a pure ketal of the diol. The isolation of a cyclic ketal shows that the carbomethoxy and carboxaldehyde functions of the hydroformylated product must have the cis relationship. Further confirmation of the cis relationship was obtained by converting the hydroformylation product to the diacid and measuring the acid dissociation constants, K_1 and K_2, of this diacid. The ratio K_1/K_2 is approximately 200 whereas for the trans isomer a ratio of 20–50 would be expected.[2] The ^{1}H NMR spectrum of the hydroformylated product did not permit us to distinguish unambigously (J^3 = 7.3 Hz) between **2** and **4**. Decarbonylation of the hydroformylated product to a compound of known stereochemistry[3] using [RhCl(PPh$_3$)$_3$] was unsuccessful and so it was decided to synthesize **2** and **4** (or appropriate precursors) for comparison purposes.

The syntheses of lactone **12** and diol **14** of the *trans*-1,2-diphenylcyclopropane, compounds which could be related to **4**, are described in Scheme I. Because both the lactone and the diol were found to be different from those derived from the hydroformylated product of **1**, the isomeric lactone **13** and diol **15** having the phenyl groups cis were synthesized via Scheme I, starting with the cinnamyl alcohol **7**. Lactone **13** and diol **15** proved to be identical with the corresponding compounds derived from the hydroformylated product. The hydroformylated product **2** on treatment with NaBH$_4$ in MeOH/THF for 5 h at 0 °C gives a lactone identical with **13**, and further reduction with LiAlH$_4$ gives a diol identical with synthetic **15**. Finally lactone **13** is converted to the hydroformylation product **2**. The formation of **2** as the exclusive hydroformylation



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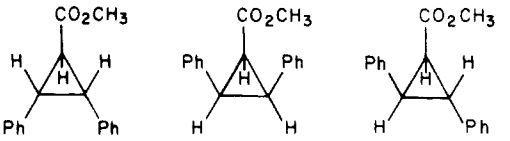
product of **1** is consistent with concerted cis addition of HCo(CO)$_4$ to the more hindered face of **1**.

Workup of the mother liquor remaining after the isolation of **2** led to the identification of three products corresponding to the hydrogenation products of **2**. The structures of these isomers and the percentage of each in the total hydrogenated product are shown below. The



48.8% 39.3% 11.9%

indicated percentages correspond to a total of about 88% cis addition; the major hydrogenation product resulted from cis addition at the more hindered face of **1** as was the case for hydroformylation.

Experimental Section

Stoichiometric Hydroformylation of 1. In a typical reaction, 1.2 g (4.8 mmol) of **1**[4] in 85 mL of hexane was treated with 9.8 mmol of dry HCo(CO)$_4$[5] in 33 mL of hexane. The reaction was carried out at room temperature with stirring in a CO atmosphere. The reaction commenced immediately and was accompanied by CO absorption. After about 15 min a precipitate appeared and after about 1.5 h the solution was filtered. The solid was recrystallized from hot hexane and had mp 144.5–145.0 °C. Anal. Calcd for C$_{17}$H$_{16}$O$_3$: C, 77.13; H, 5.75. Found: C, 76.63; H, 5.70. The IR spectrum showed two carbonyl bands at 1710 (CHO) and 1735 cm^{-1} (CO$_2$CH$_3$). The ^{1}H NMR (60-MHz Varian T 60) spectrum in CDCl$_3$ showed the following peaks: δ 9.85 (s, 1, CHO), 7.13 (m, 10, 2 phenyls), 3.85 (s, 3, CO$_2$CH$_3$), 3.80 (d, 1, cyclopropyl, J^3 = 7.3 Hz), 3.22 (d, 1, cyclopropyl, J^3 = 7.3 Hz). This compound proved identical (melting point, mixture melting point, ^{1}H MMR spectrum) with the one synthesized by the unambiguous procedure described below.

The filtrate obtained after removal of **2** was cooled to −20 °C and a small amount of additional **2** removed by filtration. The filtrate was allowed to stand in air several days and was filtered from precipitated cobalt salts, and the filtrate was washed with dilute HCl. The organic layer was separated, dried, and evaporated, leaving 0.415 g of an oily mixture of the three hydrogenated isomers. Analysis of the ^{1}H MMR spectrum of the mixture by comparison with the spectra of the known[6] isomers, especially the chemical shifts of the carbomethoxy protons,[7] showed the

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isomers to be present in the proportions indicated in the text above.

Conversion of Hydroformylation Product to a 2,3-Diphenyl-1,2-cyclopropanedicarboxylic Acid. Approximately 20 mg of the hydroformylated product was dissolved in alcoholic NaOH and warmed to 60 °C and the solution treated dropwise with $KMnO_4$ solution until color persisted. The solution was then refluxed for 12 h and filtered. The filtrate was cooled to 0 °C and acidified with HCl to pH 3. The product was extracted with CH_2Cl_2, and the solution was then dried and evaporated to dryness, leaving about 20 mg of crystalline material. Recrystallization from CH_2Cl_2 gave the diacid *cis*-2,3-diphenyl-*cis*-1,2-cyclopropanedicarboxylic acid: mp 151–153 °C; neutral equivalent theoretical 287, found 283. The IR spectrum (mull) showed strong OH absorption and two carbonyl bands (1610 and 1700 cm^{-1}). The ^1H NMR spectrum (60-Hz Varian A60) in CCl_4 showed δ 7.13 (m, 10, 2 phenyls), 3.10 (s, 1), and 2.90 (s, 1) for the cyclopropane hydrogens (J^3 = 7.4 Hz). The diacid was titrated with 0.01 N NaOH, using a pH meter, and the difference between the two pK_a values was greater than 2.

Conversion of the Hydroformylation Product via Diol 15 to the Ketal of 15. A solution of 100 mg of the hydroformylation product in 50 mL of ether was added dropwise to a stirred suspension of 1.0 g of $LiAlH_4$ in 50 mL of ether. After being refluxed for 1 h the mixture was treated with a saturated aqueous solution of potassium sodium tartrate. The ether layer was separated, dried, and evaporated. The solid residue was recrystallized from CH_2Cl_2/C_5H_{12} to give 81 mg (88.6%) of pure diol **15**: mp 121–122 °C; IR (KBr) 3280 (s), 1500 (m), 1460 (m), 1450 (m), 1060 (m), 1025 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00 (m, 10, phenyls), 4.20 (m, 2, oxymethylene), 3.70 (m, 2, oxymethylene), 2.80–3.40 [br s, 2 (disappears with D_2O), OH], 2.25 (m, 2, cyclopropyl methines). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.31; H, 7.09. Found: C, 80.10; H, 7.23.

A solution of 50 mg of diol **15** (derived from the hydroformylated product as above) and 5 mg of TsOH in 5 mL of $CH_3C(OCH_3)_2CH_3$ was allowed to stand at room temperature for 2 h. The mixture was diluted with 100 mL of ether and the resulting solution washed with 5% $NaHCO_3$ solution and water. The solution was dried and evaporated in vacuo at room temperature. The residue was chromatographed on alumina, using hexane as the eluant. Removal of the solvent gave 46.4 mg (80.3%) of a viscous oil; ^1H NMR ($CDCl_3$) δ 6.9 (m, 10, 2 phenyls), 4.05 (m, 4, methylenes), 2.75 (d, 1, benzylic methine), 2.15 (m, 1, methine), 1.35 (s, 6, CH_3). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.30; H, 7.76.

Attempted Decarbonylation of Hydroformylation Product. A mixture of 30 mg of hydroformylation product and 99 mg of $RhCl(PPh_3)_3$ in 5 mL of xylene was stirred and refluxed for 12 h. The residue obtained on evaporation was treated with 200 mL of boiling hexane and the hexane solution evaporated. The residue proved to be Ph_3PO. The ^1H NMR and the IR spectra of the insoluble material could not be successfully interpreted and the reaction was abandoned.

***(Z)*-2,3-Diphenylpropenal (*cis*-α-Phenylcinnamaldehyde).** To a solution of 25 g (0.122 mol) of *cis*-α-phenylcinnamylnitrile[8] in 1.2 L of dry toluene was added 134 mL (0.134 mol) of 1 M diisobutylaluminum hydride in hexane during a 30-min period with stirring at −65 °C. After the addition of the hydride was complete, the solution was stirred for an additional 30 min at −65 °C and then allowed to come to room temperature over a 2-h period. The solution was then shaken with 600 mL of saturated aqueous NH_4Cl for 30 min, then 480 mL of 5% H_2SO_4 was added, and the entire mixture shaken for 10 s. The phases were separated; the aqueous phase was extracted with 400 mL of ether and combined with the organic phase. The organic phase was washed with H_2O and saturated NaCl solution and then evaporated. The residual yellow oil was taken up in 400 mL of ether, and the ether solution was dried and evaporated. The remaining oil was dissolved in 350 mL of hot hexane–CH_2Cl_2 (90/10). When the mixture was cooled, 11.5 g of crude product crystallized. Recrystallization from hexane–CH_2Cl_2 gave 9.5 g (37.4%) of a cream colored powder: mp 119.5–120.5 °C; IR ($CHCl_3$) 2860 (w), 1680 (s), 1500 (w), 1450 (w), 1345 (w), 1060 (w), 930 (w), cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.17 (s, 1, aldehyde), 7.90 (s, 1, vinyl), 7.43 (s, 10, phenyls). Anal. Calcd for $C_{15}H_{12}O$: C, 86.72; H, 5.91. Found: C, 86.51; H, 5.81.

***(Z)*-2,3-Diphenylpropen-1-ol (*cis*-α-Phenylcinnamyl Alcohol), 6.** To a solution of 20 g (0.1 mol) of the cinnamylaldehyde in 80 mL of hot THF was added 600 mL of dry Et_2O. The solution was cooled to −10 °C and a suspension of 1.30 g (0.034 mol) of $LiAlH_4$ in 60 mL of Et_2O was added at a rate such that the temperature did not exceed 0 °C. After the addition, the temperature was allowed to rise to 10 °C and then 20 mL of H_2O was slowly added. The suspension was filtered through Celite and evaporated to 200 mL. After being washed with H_2O and saturated NaCl, the solution was dried over $CaCl_2$ and the solvent was evaporated, leaving a yellow-orange residue which solidified on standing. Recrystallization from hot hexane gave 17.4 g (82.8%) of colorless crystals: mp 75–77 °C (lit.[9] mp 74–75 °C); IR (KBr) 3400 (s), 1595 (w), 1490 (w), 1445 (m), 1080 (m), 1050 (s), 1035 (s), 775 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4 (m, 10, phenyls), 6.95 (s, 1, vinyl), 4.6 (s, 2, methylene), 1.9 (s, 1, dissappears with D_2O, OH).

***(E)*-2,3-Diphenylpropen-1-ol (*trans*-α-Phenylcinnamyl Alcohol), 7.** To a refluxing solution of 25 g (0.11 mol) of *trans*-α-phenylcinnamic acid in 1 L of anhydrous ether was slowly added a suspension of 8.36 g (0.22 mol) of $LiAlH_4$ in 500 mL of ether. After the addition, the solution was refluxed for an additional 1 h. The solution was cooled and 20 mL of H_2O was slowly added. The suspension was then washed with a mixture of 300 mL of saturated NH_4Cl and 300 mL of 5% H_2SO_4 followed by washings with H_2O and saturated NaCl. The solvent was evaporated to 200 mL and the solution was dried over $MgSO_4$. The solvent was then further evaporated, leaving a yellow oil which solidified on standing. Recrystallization from hot hexane gave 20.0 g (85%) of white crystals: mp 66–68 °C (lit.[4] mp 68–69 °C); IR (CCl_4) 3390 (s), 1492 (s), 1443 (m), 1088 (m), 1028 (s), 915 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15 (5, s, phenyl), 6.95 (5, s, phenyl), 6.80 (1, s, vinyl), 4.30 (2, s, methylene), 2.78 (s, 1, disappears with D_2O, OH).

***cis*-α-Phenylcinnamyl Acetoacetate, 8, and *trans*-α-Phenylcinnamyl Acetoacetate, 9.** Under dry nitrogen, 32.0 g (0.153 mol) of *trans*-α-phenylcinnamyl alcohol and 37.5 g (0.17 mol) of acetyl Meldrum's acid[10] were refluxed in 75 mL of dry benzene for 20–30 h. The cooled solution was filtered and the solvent evaporated, leaving a brown oil. The oil was placed on an 8 × 2.5 in. column of silica gel (70–230 mesh) and eluted with $CHCl_3$. The desired product was eluted first, leaving starting material and impurities at the top of the column. The solvent was evaporated, leaving a viscous yellow oil, weighing 44 g (96–100%), of 98% pure *trans*-α-phenylcinnamyl acetoacetate, **9** (^1H NMR). The same yields were obtained for *cis*-α-phenylcinnamyl acetoacetate, **8**. *trans*-α-Phenylcinnamyl acetoacetate, **9**: IR (thin film) 1746 (s), 1720 (s), 1647 (w), 1497 (w), 1448 (m), 1150 (s), 1025 (m), 760 (m), 700 (s); ^1H NMR ($CDCl_3$) δ 7.23 (s, 5, phenyl), 7.03 (s, 5, phenyl), 6.72 (s, 1, vinyl), 4.98 (s, 2, oxymethylene), 3.37 (s, 2, carbonyl methylene), 2.03 (s, 3, carbonyl methyl). *cis*-α-Phenylcinnamyl acetoacetate, **8**: IR (thin film) 1740 (s), 1710 (s), 1485 (w), 1435 (w), 1350 (w), 1300 (w), 1140 (s), 1020 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40 (m, 10, phenyls), 7.10 (s, 1, vinyl), 5.21 (s, 2, oxymethylene), 3.35 (s, 2, carbonyl methylene), 2.03 (s, 3, carbonyl methyl).

***cis*-α-Phenylcinnamyl Diazoacetate, 10, and *trans*-α-Phenylcinnamyl Diazoacetate, 11.** In a 5-L flask were placed 2 L of benzene, 50 g (0.17 mol) of *trans*-α-phenylcinnamyl acetoacetate, 36 g (0.18 mol) of tosyl azide, 4.0 g of $(CH_3)_4NBr$, and 54 mL (0.54 mol) of 10 N NaOH. The mixture was stirred very vigorously with a mechanical stirrer for 48–54 h at room temperature. The solution was washed with 1 L of H_2O, 700 mL of 2.5% NaOH, and again with 1 L of H_2O before drying over $CaCl_2$. The solvent was evaporated, leaving a viscous yellow oil.

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The oil was redissolved in 400 mL of ether and washed again with 2.5% NaOH and H_2O before drying over $CaCl_2$. The solvent was evaporated, leaving 42 g of viscous oil. The oil was found (^1H NMR) to be a mixture of about 60% product, **11**, 30% *trans*-α-phenylcinnamyl alcohol, and 10% *trans*-α-phenylcinnamyl diazoacetoacetate. Product **11** was separated by chromatography, using a 21 × 2 in. column of silica gel (70–230 mesh) with $CHCl_3$ eluant. The product, **11**, which was eluted first, was isolated as a yellow oil, 22 g (47%). The same results were obtained in the preparation of **10**. *trans*-α-Phenylcinnamyl diazoacetate, **11**: IR (thin film) 2060 (vs), 1700 (vs), 1495 (m), 1445 (m), 1390 (vs), 1345 (vs), 1235 (vs), 1175 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.21 (s, 5, phenyl), 7.02 (s, 5, phenyl), 6.65 (s, 1, vinyl), 4.98 (d, 2, J^3 = 1 Hz, oxymethylene), 4.65 (s, 1, diazomethine). *cis*-α-Phenylcinnamyl diazoacetate, **10**: IR (thin film) 2055 (vs), 1689 (vs), 1390 (vs), 1370 (vs), 1360 (vs), 1240 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42 (m, 10, phenyls), 7.15 (s, 1, vinyl), 5.30 (s, 2, oxymethylene), 4.72 (s, 1, diazomethine).

Lactones 12 and 13. To a refluxing 2-L solution of dry, alcohol-free, benzene, containing 30 g of anhydrous $CuSO_4$, was added a solution of 16.0 g (0.0557 mol) of *trans*-α-phenylcinnamyl diazoacetate, **11**, in 100 mL of benzene, over a 1-h period. The solution was then refluxed further for 4 h. The cooled solution was filtered, and the solvent evaporated to a yellow oil. The oil was redissolved in 250 mL of ether and washed with two 200-mL portions of H_2O before drying over $MgSO_4$. The solvent was evaporated, leaving 19.3 g of an oil consisting of lactone **13** as the minor product, *trans*-α-phenylcinnamyl cycloheptatrienyl-1-carboxylate [(*E*)-2,3-diphenyl-2-propenyl 2,4,6-cycloheptatrienyl-1-carboxylate] as the main product, and a small amount of unidentifiable material (column chromatography and ^1H NMR). Lactone **13** was recrystallized from hexane–$CHCl_3$, giving 1.73 g (11.8%) of white crystals, mp 124–125 °C. Lactone **12** was prepared in the same manner, yielding an oil in yields of 6–10%. Lactone **13**: IR (KBr) 1762 (s), 1500 (m), 1448 (m), 1350 (m), 1165 (s), 1012 (s), 910 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00 (m, 10, phenyls), 4.65 (d, J^3 = 8–9 Hz, 1, oxymethylene), 4.35 (d, J^3 = 8–9 Hz, 1, oxymethylene), 2.85 (d, J^3 = 3 Hz, 1, cyclopropyl methine), 2.75 (d, J^3 = 3 Hz, 1, cyclopropyl methine). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.71; H, 5.74. Lactone **12**: colorless oil; IR (thin film) 1775 (vs), 1502 (m), 1453 (m), 1175 (m), 1035 (s), 935 (m), 765 (m), 703 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (s, 10, phenyls), 4.45 (d, J^3 = 9–10 Hz, 1, oxymethylene), 4.30 (d, J^3 = 9–10 Hz, oxymethylene), 3.15 (d, J^3 = 9 Hz, 1, cyclopropyl methine), 2.80 (d, J^3 = 9 Hz, 1, cyclopropyl methine).

Diols 14 and 15. To a refluxing solution of 35 mg (0.9 mmol) of $LiAlH_4$ in 10 mL of anhydrous ether was added slowly 300 mg (1.2 mmol) of lactone **13** in 7 mL of ether. After the addition was complete, the solution was refluxed for 1 h. After the solution was cooled, 1 mL of H_2O was added slowly followed by dilution with 50 mL of ether. The suspension was then washed successively with two 50-mL portions of saturated NH_4Cl, three 50-mL portions of H_2O, and 50 mL of saturated NaCl before drying over $MgSO_4$. The solvent was evaporated and the residue recrystallized from hexane–CH_2Cl_2, giving 200 mg (66%) of white needles, mp 122.5–124.5 °C. This diol was identical with the diol prepared from the hydroformylation product. Diol **14** was prepared in the same manner; the product, however, was an oil and had to be purified by preparative TLC (30% yield): IR (thin film) 3350 (s), 1500 (s), 1450 (s), 1145 (w), 1025 (vs), 910 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (m, 10, phenyls), 3.98 (m, 2, methylene), 3.45 (m, 4, oxymethylene and OH's), 2.65 (d, J^3 = 9 Hz, 1, cyclopropyl methine), 2.00 (m, 1, cyclopropyl methine).

Methyl *c*-2-(Hydroxymethyl)-*t*,*t*-2,3-diphenylcyclopropane-*r*-1-carboxylate, 16. A solution of 1.56 g (6.24 mmol) of lactone **13** and a crystal of *p*-toluenesulfonic acid in 100 mL of dry methanol was stirred for 2 days. The solvent was evaporated to 10 mL, then dissolved in 100 mL of $CHCl_3$, and washed with two 100-mL portions of H_2O before drying over $MgSO_4$. The solvent was evaporated, leaving a colorless oily residue. The residue was shown (^1H NMR) to be 30% product **16** and 70% starting lactone **13**. Apparently an equilibrium exists between the lactone and the open hydroxy ester product. The product was separated by chromatography on a 0.75 × 12 in. column of silica gel (10–230 mesh) with $CHCl_3$ as eluant. The starting lactone elutes first, followed by the product, **16** (0.535 g, 30% conversion, 98% yield). The recovered lactone was treated a second time, as above, and 0.34 g of additional **16** and 0.71 g of lactone **13** were obtained at the same levels of conversion and yield. Recrystallization from hexane gave white crystals: mp 93–94 °C; IR ($CHCl_3$) 3480 (m), 1728 (s), 1602 (w), 1498 (w), 1442 (s), 1302 (m), 1065 (w), 1025 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00 (m, 10, phenyls), 4.10 (br s, 2, methylene), 3.80 (s, 3, carbomethoxy methyl), 3.15 (d, J^3 = 6–7 Hz, 1, cyclopropyl methine), 2.70 (d, J^3 = 6–7 Hz, 1, cyclopropyl methine), 2.45 (br s, 1, disappears with D_2O, OH). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.60; H, 6.38. Found: C, 76.76; H, 6.53.

Methyl *t*,*t*-2,3-Diphenyl-*c*-2-formylcyclopropane-*r*-1-carboxylate, 2. A mixture of freshly prepared MnO_2 and 300 mg (1.06 mmol) of **16** in 25 mL of dry CH_2Cl_2 was stirred for 22 h at room temperature. The suspension was filtered and the MnO_2 was washed with six 75-mL portions of CH_2Cl_2. The CH_2Cl_2 washings and the original CH_2Cl_2 solution were combined and filtered through a Celite bed. Evaporation of the solvent gave 142 mg of a yellow residue. The residue was shown (^1H NMR) to be a mixture of 70% lactone **13** (see equilibrium discussed for **16** preparation) and 30% product **2**. Since the TLC R_f values for **16** and **2** are very similar for a wide range of solvent mixtures, the product, **2**, could not be separated by column chromatography or preparative TLC. Pure **2** was finally obtained by five fractional recrystallizations from hexane–$CHCl_3$, giving 10 mg (3%), mp 146–148 °C (mixture melting point with hydroformylated cyclopropene was 146–148 °C). The ^1H NMR ($CDCl_3$) spectrum was identical with that of **2** isolated from the hydroformylation of **1**.

Preparation of Lactone 13 via the Hydroformylated Cyclopropene 2. In 3 mL of hot THF was dissolved 226 mg (0.8 mmol) of **2** (prepared via the hydroformylation of cyclopropene **1**) followed by 3 mL of dry methanol. At 0 °C, 20 mg (0.6 mmol) of $NaBH_4$ was added and the solution was maintained at 0 °C for 5 h with stirring. The solution was then diluted with 50 mL of $CHCl_3$ and washed with 50 mL of 5% HCl and 50 mL of saturated NaCl before drying over $MgSO_4$. The solvent was evaporated, giving 142 mg (68.3%) of a white residue. The ^1H NMR spectrum showed it to be 100% lactone **13**. Recrystallization from hexane–$CHCl_3$ gave mp 124–125.5 °C (mixture melting point with the independently synthesized **13**, 124–125.5 °C).

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Registry No. **1**, 7576-36-5; **2**, 77060-83-4; **6**, 2699-89-0; **7**, 22835-64-9; **8**, 77060-84-5; **9**, 77060-85-6; **10**, 77060-86-7; **11**, 77060-87-8; **12**, 77060-88-9; **13**, 77096-70-9; **14**, 77060-89-0; **15**, 77096-71-0; **15** ketal, 77060-90-3; **16**, 77060-91-4; *cis*-2,3-diphenyl-*cis*-1,2-cyclopropanedicarboxylic acid, 77060-92-5; (*Z*)-2,3-diphenylpropenal, 72659-45-1; *cis*-α-phenylcinnamylnitrile, 6114-57-4; *trans*-α-phenylcinnamic acid, 91-48-5; $HCo(CO)_4$, 16842-03-8.