3-*tert*-Butoxy-5-butyl-2,5-cyclohexadiene-1,4-dione (7f). 2-Lithiohexene (2-bromohexene in THF, -78 °C, 2 equiv of *t*-BuLi) addition to **2**, reflux in toluene (25 min), followed by oxidation and purifiaction by flash column chromatography of silica gel (8:1 hexane/ethyl acetate) provided **7f** (52 mg, 58%) as a bright yellow oil: IR ($CHCl_3$, cm^{-1}) 1675, 1651; ^1H NMR ($CDCl_3$ δ 6.40 (m, 1 H), 5.99 (d, J = 2.4 Hz, 1 H), 1.50 (s, 9 H),; ^{13}C NMR ($CDCl_3$) δ 188.0, 183.0, 155.3, 147.6, 132.2, 110.7, 82.3, 29,7, 28.6, 27.7, 22.2, 13.7.

2-*tert*-Butoxy-5-methyl-2,5-cyclohexadiene-1,4-dione (7g). Into dry THF (3 ML), cooled to -78 °C under Ar, was condensed propyne gas for 30 s. *n*-BuLi (0.43 mL of a 1.2 M solution in hexane, 0.52 mmol) was added, and the resulting solution was stirred for 30 min. the anion was then added via cannula to a -78 °C solution of dione **2** (66 mg, 0.43 mmol) in dry THF (12 mL). After stirring another 30 min the solution was poured into NH_4Cl (10%, 20 mL). The aqueous layer was extracted with ethyl acetate (2 × 30 mL), and the organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and evapoarated to a light yellow oil (81 mg, 96%). The alcohol was unstable at rt, but the following spectroscopic data were obtained: IR ($CHCl_3$, cm^{-1}) 1760, 1567; ^1H NMR ($CDCl_3$) δ 5.26 (s, 1 H), 1.89 (s, 3 H), 1.54 (S, 9 H).

The alcohol in dry acetonitrile (40 mL) was heated at reflux under Ar for 30 min. Upon cooling and evaporation of the solvent the quinone was purified by flash column chromatography on silica gel (4:1 hexane/ethyl acetate) to yield **7g** (53 mg, 66%) as bright yellow plates: IR ($CHCl_3$, cm^{-1}) 1678, 1652; ^1H NMR ($CDCl_3$) δ 6.51 (q, J - 1.5 Hz, 1 H), 6.06 (s, 1 H), 2.01 (d, J = 1.5 Hz, 3 H), 1.52 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 188.1, 183.2, 155.3, 145.9, 131.7, 111.3, 82.5, 27.8, 15.6.

2-*tert*-Butoxy-5-butyl-2,5-cyclohexadiene-1,4-dione (7h). The preceding procedure was followed using 1-lithiohexyne (1-hexyne, -78 °C, *n*-BuLi), which gave the intermediate alcohol (91%) as a white solid that was unstable at rt: ^1H NMR ($CDCl_3$) δ 5.25 (s, 1 H), 1.52 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 187.0, 181.9, 113.4, 90.8, 86.4, 85.3, 73.9, 30.2, 27.4, 21.8, 18.6, 13.5.

The alcohol was heated at reflux in acetonitrile for 1 h under Ar and purified as above to yield **7h** as a bright yellow solid (53 mg, 61%): IR ($CHCl_3$, cm^{-1}) 1672, 1646; ^1H NMR ($CDCl_3$) δ 6.45 (t, J = 1.4 Hz, 1 H), 6.04 (s, 1 H), 1.51 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 187.9, 183.4, 155.1, 149.7, 130.7, 111.4, 82.4, 29.9, 28.5, 27.8, 22.4, 13.8.

6-*tert*-Butoxy-5-(phenylthio)-4,7-benzofuranquinone (12). Quinone **7d** (9.3 mg, 0.042 mmol) was placed in dry THF/ethanol (1:1, 1 mL) under Ar. Thiophenol (9 μL, 0.084 mmol) was added, and the reaction mixture was allowed to stir for 30 min. After evaporation of the solvent the yellow oil was dissolved in benzene (2 mL), and Ag_2O (39 mg, 0.17 mmol) and anhydrous K_2CO_3 (23 mg, 0.17 mmol) were added. The suspension was stirred for 4 h at rt, filtered through Celite, and evaporated. The crude product was eluted through a column of silica gel (5:1 hexane/acetone) to give **12** (13 mg, 93%) as a dark red oil: IR ($CHCl_3$, cm^{-1}) 1675; ^1H NMR ($CDCl_3$) δ 6.81 (d, J = 1.8 Hz, 1 H), 1.53 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 178.0, 171.0, 158.0, 148.5, 135.5, 134.3, 130.3, 129.0, 128.9, 127.5, 127.1, 127.0, 108.8, 29.6.

2-Hydroxy-1,4-phenanthrenedione (13). To trifluoroacetic acid (4 mL), cooled to 0 °C, was added quinone **7a** (34 mg, 0.12 mmol). The resulting yellow solution was stirred for 15 min at 0 °C, during which time the solution turned orange. The acid was evaporated with toluene (2 × 5 mL), and the orange powder was recrystallized (acetone/hexane) to yield **13** as an orange powder (26 mg, 95%): IR (acetone-d_6, cm^{-1}) 1630, 1585; ^1H NMR (acetone-d_6) δ 6.37 (s, 1 H), 3.05 (bs, 1 H, exchangeable with D_2O); ^{13}C NMR (acetone-d_6) δ 185.3, 184.3, 159.0, 136.4 (2), 133.7, 130.6, 130.1, 129.4, 128.6, 127.2, 125.1, 122.0, 108.0.

Lawsone (14). Lawsone was prepared from **7b** as described above to provide **14** (20 mg, quant. yield) as a bright yellow solid identical with the natural product:[7a] IR (CH_2Cl_2 cm^{-1}) 1658, 1595; ^1H NMR (acetone-d_6) δ 6.23 (s, 1 H), 3.08 (bs, 1 H); ^{13}C NMR ($CDCl_3$) δ 183.3, 180.2, 157.2, 133.3, 131.8, 131.3, 129.2, 124.7, 124.5, 109.5.

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Supplementary Material Available: Full experimental section and ^{13}C and/or ^1H NMR spectra for compounds **2**, **7a-h**, **8g**, **8h**, 11-14 (33 pages). Ordering information is given on any current masthead page.

A Remarkable Short Synthesis of Optically Active Mevinic Acid Analogues by Biocatalytic Lactonization of *syn*-3,5-Dihydroxy Esters[1]

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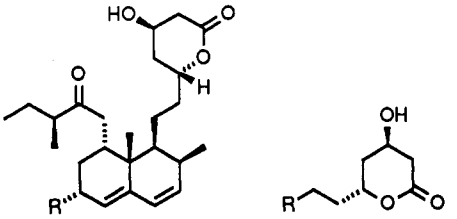
Since the discovery of compactin and mevinolin[2] as potent inhibitors of HMG-CoA reductase, many asymmetric or racemic synthetic approaches to these compounds have appeared.[3] Despite its rather simple structure, the lactone moiety of the mevinic acids has proved to be essential for the biological activity of such compounds.[4]

For these reasons, many efforts have been made to discover and synthesize new analogues of type 1 with different R substituents.[5] In some cases such analogues have proven to be more effective than the natural mevinic acids.



R = H; compactin
R = CH_3; mevinolin

1

Nevertheless, the synthesis of these compounds in optically pure form has turned out to be rather challenging, and it was always achieved in several steps either by means of asymmetric reactions or starting from optically active natural products.[6]

In principle (see Scheme I) the target lactone **1** could be directly prepared from the *syn*-1,3-diol ester A, which can be obtained by the diastereoselective reduction[7] of

(1) Presented at 8th IUPAC Conference on Organic Synthesis. Helsinki, July 23-27, 1990.

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(3) For a review, see: Rosen, T.; Heathcock, C. A. *Tetrahedron* **1986**, *42*, 4909.

(4) Stokker, G. E.; Hoffman, W. F.; Alberts, W.; Cragoe, E. J., Jr.; Deana, A. A.; Gilfillan, J. L.; Huff, J. W.; Novello, F. C.; Prugh, J. D.; Smith, R. L.; Willard, A. K. *J. Med. Chem.* **1985**, *28*, 347.

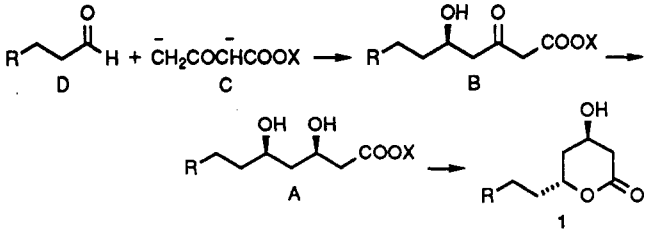
(5) (a) Willard, A. K.; Novello, F. C.; Hoffman, W. F.; Cragoe, E. J. U.S. Patent 4,375,473, 1983. (b) Kathawala, F. G. PCT Int. Appl. WO 84 02, 131; *Chem. Abstr.* **1985**, *102, 24475j*. (c) Lynch, J. E.; Volante, R. P.; Wattley, R. V.; Shinkai, I. *Tetrahedron Lett.* **1987**, *28*, 1385. (d) Baader, E.; Bartmann, W.; Beck, G.; Bergmann, A.; Jendralla, H.; Kesseler, K.; Wess, G.; Schubert, W.; Granzer, E.; Kerekjarto, B. V.; Krause, R. *Ibid.* **1988**, *29*, 929.

(6) For a list of most asymmetric syntheses, see: David, D.; Gesson, J. P.; Jacquesy, J. C. *Tetrahedron Lett.* **1989**, *30*, 6015 and references therein.

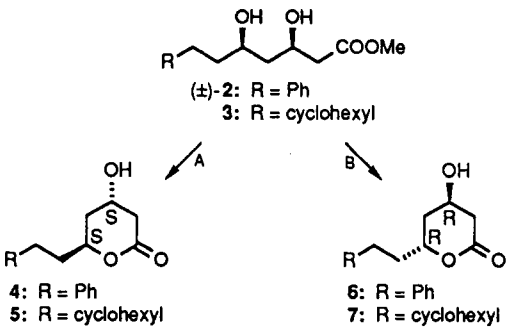
(7) Many procedures are available for the diastereoselective reduction of β-hydroxy ketones or keto esters to *syn*-1,3-diols. For up-to-date papers, see: (a) Evans, D. A.; Hoveyda, A. H. *J. Org. Chem.* **1990**, *55*, 5190 and a complete list of references therein enclosed. (b) Bonini, C.; Bianco, A.; Di Fabio, R.; Mecozzi, S.; Righi, G.; Proposito, A. *Gazz. Chim. Ital.* **1991**, *121*, 75.

0022-3263/91/1956-4050$02.50/0

Scheme I



Scheme II



aldol B. The latter can simply be prepared by direct aldol condensation of the dianion of acetoacetate C with an appropriate aldehyde D.[8] In this sequence, an enantiospecific step is needed to obtain optically pure compounds.

In fact, we discovered that such a strategy is possible by simply performing the enantioselective lactonization of A to the target compound 1.

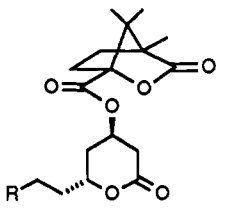
Recently some methods have been developed by means of which it is possible to achieve the biocatalytic lactonization of simple hydroxy esters, both in aqueous or organic solution.[9,10] Therefore we have tried to carry out the enzymatic enantioselective lactonization of two (±)-dihydroxy esters (2 and 3), which possess the two hydroxy groups in the desired syn configuration. This way, it was hoped that the corresponding mevinic acid analogues 4, 5, or 6, 7, that we and others previously synthesized by following different routes,[11] could be obtained.

The starting *syn*-3,5-dihydroxy esters 2 and 3 were prepared respectively from phenylpropionaldehyde and cyclohexylpropionaldehyde with the dianion of methyl acetoacetate (see Scheme I); the subsequent diastereoselective reduction of the aldols of type B to the syn diols of type A was performed as described in ref 7b; the reaction sequence afforded the purified compounds 2 and 3 in a 57–61% overall yield. All the compounds showed consistent spectroscopic and analytical data (see experimental).

As described in Scheme II, two different reaction conditions were chosen to perform the biocatalytic lactonization of 2 and 3, and the results were very promising. Under condition A (aqueous solution with PLE) the reaction (monitored by HPLC) was very fast and was stopped after 3 h.[12] The resulting lactonization of 2 and 3 afforded the corresponding 4 and 5 (3*S*,5*S* as showed by the sign of the optical rotation, see the Experimental Section) with an 80% chemical yield (based on the conversion) and an enantiomeric excess of 33% (for compound 4) and of 50% for compound 5. In addition the starting dihydroxy esters were completely recovered.

Much better results were obtained using condition B, based on the pioneering work by Klibanov[13] (PPL in ether solution). The reaction was considerably slower both for 2 and 3 and was stopped after 96 h (40% of conversion). The resulting purified lactones 6 and 7 (3*R*,5*R*, having the same configuration as the natural mevinic acids) were enantiomerically pure (ee >98%) and obtained with a 70% chemical yield based on the conversion and the substantial recovery of the starting materials.

The enantiomeric excess for all the lactones 4–7 was determined on the derivatives prepared with (−)-camphanic acid chloride[14] using HPLC and ^{1}H NMR experiments (see structure for a representative example of compound 8 with R = cyclohexyl or phenyl, reported in the Experimental Section).



8a: R = Ph
8b: R = cyclohexyl

All the lactones 4–7 have the same spectroscopic and analytical properties as described in ref 11.

Interestingly the stereospecificity of the reactions were markedly different, depending on the condition used: with PLE the 3*S*,5*S* enantiomers, both for 2 and 3, are preferred, while PPL highly preferred the 3*R*,5*R* enantiomers.

A lactonization procedure for the *anti*-1,3-diol esters is now under investigation.

Although this biocatalytic lactonization needs to be studied in more detail, especially with respect to the effect of the side chain substituents, the three-step synthesis described represents, by far, the shortest entry into a biologically important class of optically active compounds. Along these lines, further experiments are in progress. The aim of this work is not only that to better study the kinetics of the enantiospecific lactonization under different conditions, but also to apply the above methodology to the preparation of an important optically active mevinic acids analogues as well as of natural lactones and more complex polyhydroxylated esters.

Experimental Section

Flash chromatography was carried out on silica gel (70–230 mesh). TLC analyses were performed on Merck Kieselgel 60 F-254 plates. All the solvents were redistilled and dried before use.

(8) See refs 4 and 5d for similar aldehyde condensation with dianions of acetoacetate to obtain HMGCoA reductase inhibitors in racemic form.

(9) (a) Gutman, A. L.; Zuobi, K.; Boltansky, A. *Tetrahedron Lett.* **1987**, *28*, 386. (b) Makite, A.; Nihira, T.; Yamada, Y. *Ibid.* **1987**, *28*, 805. (c) Gutman, A. L.; Oern, D.; Boltansky, A.; Bravdo, T. *Ibid.* **1987**, *28*, 5367. (d) Zhi-Wei, G.; Sih, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 1999. (e) Gutman, A. L.; Bravdo, T. *J. Org. Chem.* **1989**, *54*, 4263.

(10) Only one example of biocatalytic lactonization of a hydroxy ester (methyl 5-hydroxyhexanoate) has been reported (see ref 9c), but no data on the chemical and enantiomeric yields were given.

(11) For asymmetric syntheses of compound 6 (3*R*,5*R*) see: (a) Majewski, M.; Clive, D. L. J.; Anderson, P. C. *Tetrahedron Lett.* **1984**, *25*, 2101. (b) Bonadies, F.; Di Fabio, R.; Gubbiotti, A.; Mecozzi, S.; Bonini, C. *Ibid.* **1987**, *28*, 703. (c) Roth, D. D.; Roark, W. H. *Ibid.* **1988**, *29*, 1255. (d) Johnson, C. R.; Senanayaka, C. H. *J. Org. Chem.* **1989**, *54*, 735. For asymmetric synthesis of compound 7 (3*R*,5*R*), see: (e) Rosen, T.; Taschner, M. J.; Heathcock, C. H. *J. Org. Chem.* **1984**, *49*, 3994. (f) Johnson, W. S.; Kelson, A.; Elliott, J. D. *Tetrahedron, Lett.* **1988**, *29*, 3757.

(12) In order to optimize the production of the optically active lactones, following the theory of the biocatalytic kinetic resolution, the reaction was stopped at 40% conversion and no attempts have been made, at this time, to follow the resolution up to 50% conversion in order to verify the optical purity of the remaining esters.

(13) Kirchner, G.; Scollar, M. P.; Klibanov, A. M. *J. Am. Chem. Soc.* **1985**, *107*, 7072. For a recent review, see: Klibanov, A. M., *Acc. Chem. Res.* **1990**, *23*, 114.

(14) Gerlach, H. *Helv. Chim. Acta* **1978**, *61*, 2773.

Chemical shift values are referenced to internal $CHCl_3$. Pig liver esterase (PLE EC 3.1.1.1 of type I) and crude porcine pancreatic lipase (PPL EC 3.1.1.2 of type II) were obtained from Sigma Chemical Co. and used without further purification.

General Preparation of (±)-2 and 3. To a dry THF (50 mL) solution of LDA, prepared from diisopropylamine (3.4 g, 30 mmol) and *n*-butyllithium (hexane 2.5 M solution, 12.6 mL, 31.5 mmol) was added a THF solution (8 mL) of methyl acetoacetate (1.74 g, 15 mmol) at about −78 °C under a nitrogen atmosphere. After the solution became dark red (15 min), a THF solution (6 mL) of the corresponding aldehyde (15 mmol) was added. The solution was then stirred for 20 min at −78 °C and, after TLC monitoring, quenched with a 2 N HCl solution. The mixture was then extracted with CH_2Cl_2, and the organic layer was dried over Na_2SO_4. Concentration of the solvents in vacuo afforded the crude aldols of type B (see Scheme I), which were purified by flash chromatography on silica gel.

The aldols of type B were then subjected to the diastereoselective reduction according to ref 7b.

To a THF (10 mL) solution of the aldol B (1 mmol) at about −80 °C and under a nitrogen atmosphere, $Ti(Oi\text{-}Pr)_4$ (1.1 mmol) was added, the solution was stirred for 30 min, and then an excess of $NaBH_4$ (5 mmol) was added. The reaction was completed in 1.5 h (TLC monitoring), and the mixture was then quenched with saturated NH_4Cl solution. All the organic solvents were then removed in vacuo, and the residue was extracted with AcOEt (four times). The organic layers were dried over Na_2SO_4 and concentrated in vacuo affording crude mixture of syn–anti diols (95:5), which were separated by flash chromatography. The overall yield of the two reactions was of 61% for compound **2** and of 57% for compound **3**.

Compound 2: white solid; mp 32–34 °C; ^1H NMR 1.4–1.6 (m, 2 H), 1.6–1.8 (m, 2 H), 2.38 (dd, CH_2CO, 2 H), 2.5–2.8 (m, CH_2Ph), 3.56 (s, OCH_3, 3 H), 3.73 (m, CHOH, 1 H), 4.18 (m, CHOH, 1 H), 4.4 (bs, OH, 2 H), 7.0–7.2 ppm (m, 5 H); IR (OH) 3500, (C=O) 1728 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.63; H, 7.99. Found: C, 66.49; H, 8.03.

Compound 3: white gum; ^1H NMR 0.8–0.95 (m, 2 H), 1.0–1.4 (m, 6 H), 1.5–2.0 (m, 10 H), 2.5–2.6 (m, CH_2CO, 2 H), 3.2 (bs, OH, 1 H), 3.68 (s, OCH_3, 3 H), 3.82 (m, CHOH, 1 H), 4.26 ppm (m, CHOH, 1 H); IR (OH) 3500, (C=O) 1725 cm^{-1}. Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.07; H, 10.15. Found: C, 65.01; H, 10.19.

General Procedure for Enzymatic Lactonization of Racemic 2 and 3 with Condition A (PLE). To the 3,5-dihydroxy esters **2** and **3** (0.54 mmol), suspended in a 10 mL of a 0.1 M phosphate buffer solution at pH 7.3, 30 μL of a PLE suspension in 3.2 M $(NH_4)_2SO_4$ solution were added. The addition of 1 M NaOH solution, monitored by a pH-stat (AMEL 234), proceeded until 0.4 equiv of base had been consumed (40% of conversion). The mixture was carefully acidified with 1 M HCl (pH 3–4) and immediately extracted with AcOEt (four times).

The organic layers were washed with brine until neutrality and then dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was then purified by flash chromatography (hexanes/AcOEt, 1:1, as eluent), affording the starting dihydroxy esters **2–3** (R_f = 0.6, 51%) and the lactones **4–5** (R_f = 0.5, 40%) as white solids.

Compound 4 (3*S*,5*S*): white solid; mp 74–76 °C; ^1H NMR 1.8–2.2 (m, 4 H), 2.5–3.0 (m, 4 H), 1.0–1.5 (bs, OH, 1 H), 4.36 (bs, CHOH, 1 H), 4.68 (m, CHOR, 1 H), 7.1–7.3 ppm (m, 5 H); IR 1730 cm^{-1} (C=O lactone); $[\alpha]_D$ = −15.3° *c* = 3 g/100 mL).

Compound 5 (3*S*,5*S*): white solid; mp 70–71 °C [lit. mp 69–70.5 °C (ref 4)]; ^1H NMR 0.8–1.0 (m, 2 H), 1.0–1.5 (m, 6 H), 1.5–2.0 (m, 9 H), 2.5–2.7 (m, CH_2CO, 2 H), 3.0 (bs, OH, 1 H), 4.3 (m, CHOH, 1 H), 4.62 ppm (m, CHOR, 1 H); IR 1725 cm^{-1} (C=O lactone); $[\alpha]_D$ = −11.7° (*c* = 1.45 g/100 mL).

General Procedure for the Enzymatic Lactonization of Racemic 2–3 with Condition B (PPL). PPL (200 mg) was added to a solution of the racemic compounds **2–3** (0.8 mmol) in dry ether (10 mL), and the suspension was vigorously shaken at 100 rpm at room temperature in a tightly stoppered conical flask. The reaction progress was monitored both by HPLC and ^1H NMR measurements. After 96 h (40% of the conversion) the reaction was stopped by filtering off the enzyme and washing with AcOEt. The organic solvents were then removed in vacuo, and the crude mixture was then chromatographed (hexanes/AcOEt, 1:1, as eluent), affording the starting dihydroxy esters **2–3** (48%) and the resulting lactones **6–7** (35%), which have the same ^1H NMR and IR data of compounds **4** and **5**.

Compound 6: white solid; mp 74–76 °C; $[\alpha]_D$ = +51.3° (*c* = 0.73 g/100 mL) [lit. values $[\alpha]_D$ = +45.6° (ref 12b), $[\alpha]_D$ = +68.8° (ref 12c), $[\alpha]_D$ = +46.11° (ref 12d)].

Compound 7: white solid; mp 69–70 °C; $[\alpha]_D$ = +34.1° (*c* = 0.85 g/100 mL) [lit. value $[\alpha]_D$ = +29° (ref 12f)].

Determination of the Enantiomeric Excess for Lactones 4–7: Procedure for Compounds 6 and 7. To a solution of lactone (**6** or **7**) (15 mg, 0.065 mmol) in dry pyridine (2 mL) (−)-camphanic acid chloride (0.07 mmol) was added at −10 °C. The reaction, monitored by TLC, was stopped after 4 h, diluting the mixture in ether. The organic layer was washed with 2 N HCl and then with brine until neutrality. The reaction mixtures were analyzed by ^1H NMR and HPLC before and after being purified by silica gel chromatography, showing no difference in the diastereomeric ratio. Compounds **8a** and **8b** were then purified by flash chromatography (hexanes/AcOEt, 8:2, as eluent, R_f = 0.6) and analyzed by HPLC chromatography (Merck column RP 18, with CH_3CN/H_2O, 7:3, as eluent), showing a single peak. ^1H NMR values for **8a**: 0.92 and 1.03 ppm as the only geminal methyl signals detectable (ee >98%). ^1H NMR values for **8b**: 0.86 and 0.96 ppm as the only geminal methyl signals detectable (ee >98%).

The same (−)-camphanic derivatives **8a–b** were obtained in the described condition starting from racemic lactones **6** and **7** (easily prepared by standard conditions from **2** and **3**). ^1H NMR values for the (1:1) diastereomeric mixture of **8a**: 0.90, 0.92, 1.01, and 1.03 ppm for geminal methyl signals as singlets. ^1H NMR values for the (1:1) diastereomeric mixture of **8b** 0.85, 0.86, 0.94, and 0.96 ppm for geminal methyl signals as singlets.

Acknowledgment. This work was supported by MURST, progetto "Sintesi e reattività organica"; we also thank CNR, Centro per lo Studio della Chimica delle Sostanze Organiche Naturali, Università "La Sapienza" Roma, for financial and technical assistance.

A New, Versatile Method for the Modification of Synthetic Pyrethroids: Regio- and Stereoselective Monoarylation and Heteroarylation of (2,2-Dihaloethenyl)cyclopropanecarboxylates Catalyzed by Palladium–Phosphine Complexes[1]

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The esters of (2,2-dihaloethenyl)cyclopropanecarboxylic acid (**1**) represented by permethrin (**1a**),[2] cypermethrin,[3] and deltamethrin (**1b**)[4] make up the most important part of the present household and agricultural insecticides. In the modification[5] of these synthetic pyrethroids, effort has chiefly been directed toward alcoholic parts while the acidic part, especially the dihaloethenyl moiety, has remained relatively unexplored.

Nevertheless, flumethrin (**2**),[6] a representative of pyrethroids having a partially modified ethenyl moiety,

(1) Presented in part at the 4th International Kyoto Conference on New Aspects of Organic Chemistry, Kyoto, Japan, November 14–18, 1988; Abstract, p 181.

(2) Elliot, M.; Farnham, A. W.; Janes, N. F.; Needham, P. H.; Pulman, D. A.; Stevenson, J. H. *Nature (London)* **1973**, *246*, 169.

(3) Elliott, M.; Farnham, A. W.; Janes, N. F.; Needham, P. H.; Pulman, D. A. *Pestic. Sci.* **1975**, *6*, 537.

(4) Elliott, M.; Farnham, A. W.; Janes, N. F.; Needham, P. H.; Pulman, D. A. *Nature (London)* **1974**, *248*, 710.

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