septum. CsF was added from the test tube. The reaction mixture was stirred at room temperature for the time shown in Table I and was then poured into 1.5% $NaHCO_3$ and extracted with ether. The ethereal extract was washed with 1.5% $NaHCO_3$ and then extracted with 10% HCl. The acid extract was made alkaline with NaOH and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated under reduced pressure. Kugelrohr distillation of the residual oil gave a mixture of *N,N*-dimethyl-1-(2-methylphenyl)ethylamine[4] (**4a**) and *N,N*-dimethyl-1-benzylethylamine[4] (**5a**) or of *N,N*-dimethyl-1-(5-methoxy-2-methylphenyl)ethylamine (**4b**) and *N,N*-dimethyl-1-(4-methoxybenzyl)ethylamine[4] (**5b**). The product ratios were calculated on the basis of the integrated values of the GLC analyses (2-m, 5% PEG-20M column). The yields and ratios are shown in Table I.

The ether layers remaining after extraction with 10% HCl were analyzed by GLC (5% silicone SE-30) which indicated the presence of toluene (**6a**) or 4-methoxytoluene (**6b**). The yield of **6** is calculated by comparison of the integrated values of GLC with the internal standard (propylbenzene).

***N,N*-Dimethyl-1-(5-methoxy-2-methylphenyl)ethylamine (4b)**: bp 100 °C (5 Torr); ^1H NMR ($CDCl_3$) δ 1.29 (d, 3 H, J = 7 Hz), 2.22 (s, 6 H), 2.28 (s, 3 H), 3.34 (q, 1 H, J = 7 Hz), 3.78 (s, 3 H), 6.66 (dd, 1 H, J = 9, 2 Hz), 7.00 (m, 2 H). Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.52; H, 9.98; N, 7.25.

***N,N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-2-methoxybenzylammonium Iodide (1d).** A solution of 2-methoxybenzoyl chloride (8.8 g, 52 mmol) in benzene (150 mL) was added to a stirred mixture of methyl[(trimethylsilyl)methyl]amine (6.1 g, 52 mmol) and 10% NaOH (60 mL) at room temperature, and stirring was continued for 30 min. The mixture was poured into water and extracted with ether. The ethereal extract was washed with water, dried ($MgSO_4$), concentrated, and distilled to give *N*-methyl-*N*-[(trimethylsilyl)methyl]-2-methoxybenzamide (10.9 g, 84%): bp 105–106 °C (0.09 Torr); IR (film) 1630 cm^{-1}; ^1H NMR ($CDCl_3$, 55 °C) δ 0.17 (s, 9 H), 2.84 (s, 3 H), 3.09 (bs, 2 H), 3.82 (s, 3 H), 6.89 (d, 1 H, J = 8.3 Hz), 6.97 (t, 1 H, J = 7.6 Hz), 7.22 (dd, 1 H, J = 7.6, 1.7 Hz), 7.32 (ddd, 1 H, J = 8.3, 7.6, 1.7 Hz). Anal. Calcd for $C_{13}H_{21}NO_2Si$: C, 62.11; H, 8.42; N, 5.57. Found: C, 62.05; H, 8.47; N, 5.35.

A mixture of *N*-methyl-*N*-[(trimethylsilyl)methyl]-2-methoxybenzamide (10.0 g, 40 mmol) and $LiAlH_4$ (1.5 g, 40 mmol) in ether (65 mL) was heated at reflux for 2 h. The mixture was quenched with AcOEt (60 mL), poured into 10% NaOH, and extracted with ether. The ethereal extract was dried ($MgSO_4$), concentrated, and distilled to give *N*-methyl-*N*-[(trimethylsilyl)methyl]-2-methoxybenzylamine (9.0 g, 81%): bp 128–129 °C (8 Torr); IR (film) 1245, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 1.98 (s, 2 H), 2.21 (s, 3 H), 3.47 (s, 2 H), 3.82 (s, 3 H), 6.85 (dd, 1 H, J = 7.6, 1.0 Hz), 6.93 (td, 1 H, J = 7.6, 1.0 Hz), 7.21 (td, 1 H, J = 7.6, 1.7 Hz), 7.36 (dd, 1 H, J = 7.6, 1.7 Hz). Anal. Calcd for $C_{13}H_{23}NOSi$: C, 65.77; H, 9.76; N, 5.90. Found: C, 65.74; H, 9.71; N, 5.68.

A solution of *N*-methyl-*N*-[(trimethylsilyl)methyl]-2-methoxybenzylamine (6.2 g, 26 mmol) and iodomethane (29.5 g, 208 mmol) in MeCN (80 mL) was heated at 60 °C for 1.5 h. The solvent was evaporated, and the residue was recrystallized from a mixture of AcOEt and MeOH to give **1d** (9.6 g, 97%): mp 158–159 °C; ^1H NMR ($CDCl_3$) δ 0.36 (s, 9 H), 3.28 (s, 6 H), 3.55 (s, 2 H), 3.91 (s, 3 H), 4.88 (s, 2 H), 7.00 (d, 1 H, J = 7.6 Hz), 7.07 (t, 1 H, J = 7.6 Hz), 7.49 (td, 1 H, J = 7.6, 1.3 Hz), 7.76 (dd, 1 H, J = 7.6, 1.3 Hz). Anal. Calcd for $C_{14}H_{26}NOSi$: C, 44.33; H, 6.91; N, 3.69. Found: C, 44.15; H, 7.21; N, 3.50.

***N,N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-4-nitrobenzylammonium Bromide (1k).** A mixture of 4-nitrobenzyl bromide (1.06 g, 4.9 mmol), [(dimethylamino)methyl]trimethylsilane (0.67 g, 5.1 mmol), and acetone (10 mL) was heated at reflux for 2 h. The precipitated crystals were filtered, washed with ether, and dried to give **1k** (1.65 g, 97%): mp 196–198 °C; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9 H), 3.34 (s, 2 H), 3.38 (s, 6 H), 5.46 (s, 2 H), 8.04 (d, 2 H, J = 8.7 Hz), 8.28 (d, 2 H, J = 8.7 Hz). Anal. Calcd for $C_{13}H_{23}N_2BrO_2Si$: C, 44.96; H, 6.67; N, 8.01. Found: C, 44.60; H, 6.49; N, 7.62.

Reaction of *N,N*-Dimethyl-*N*-[(trimethylsilyl)methyl]-(substituted benzyl)ammonium Halides (1c–k) with CsF. General Procedure. In a manner similar to that described for **1a,b**, an ammonium halide (2 mmol) and CsF (1.52 g, 10 mmol) were placed in a 30-mL Pyrex flask. HMPA (10 mL) was added into the flask. DBU (1.5 g, 10 mmol) was added or UV light was irradiated with a 100-W medium-pressure mercury lamp. CsF was added from the test tube, and the mixture was stirred under the conditions listed in Table II. The reaction mixture was poured into 1% $NaHCO_3$ (200 mL) and extracted with ether. The ethereal extract was washed with 1% $NaHCO_3$, dried ($MgSO_4$), and concentrated. Kugelrohr distillation of the residual oil gave a mixture of **4** and **5**. The ratio was determined from the GLC integrals.

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Highly Practical, Enantiospecific Synthesis of the Cyclohexyl Fragment of the Immunosuppressant FK-506

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In light of the increasing importance of immunosuppressive agents in clinical transplantation, the well-known FK-506, isolated from *Streptomyces tsukubaensis* (No. 9993) by Fujisawa's group,[1] has received considerable attention from synthetic as well as medicinal chemists.[2] Although the total synthesis of FK-506 has been completed by groups at Merck and Harvard,[3] efforts to develop efficient strategies for the preparation of this remarkably bioactive compound and its segments continue.[4] The cyclohexyl C28–C34 fragment of FK-506 is also a component of the related immunosuppressant rapamycin (C39–C45 fragment),[5] and the essential role of this structural unit in biological actions has recently been explored.[6] Therefore, **10** and **11** as moderately-substituted synthons of this fragment have proven to be particularly attractive targets. Several approaches, including racemic and asymmetric syntheses, have been achieved to date.[7] In this

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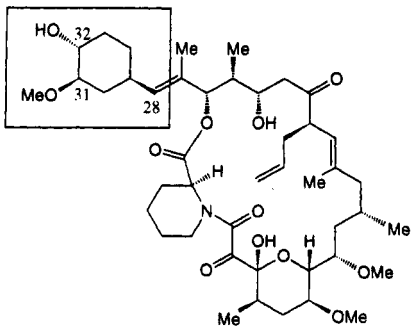
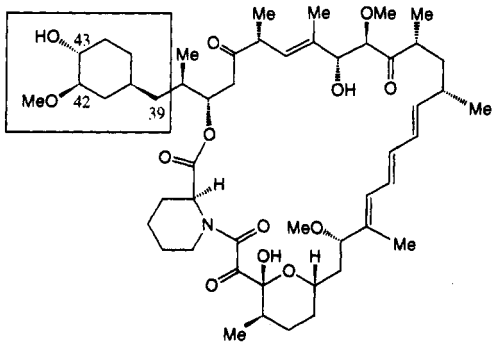


FK-506



rapamycin

paper, we describe our own approach for preparing the bicyclic lactone **10** in a completely stereo- and enantiocontrolled fashion (Scheme I).

The key intermediate lactone carboxylic acid **4** was assembled by two routes which take advantage of the relative stereochemistry at the oxygen-bearing carbon centers of either D-tartaric acid or D-mannitol. The first route relies on a powerful C–C bond-forming reaction using chiral triflate derivatives, which was developed in our laboratory.[8] Thus, triflation of diol **1**[9] followed by coupling with 2.5 equiv of *tert*-butyl lithioacetate in a mixed solvent of THF and 2,6-dimethylpropyleneurea (DMPU)[8h] at −78 °C smoothly gave the di-*tert*-butyl ester **2** ($[\alpha]^{20}_D$ = +25.4°, *c* = 1.0, $CHCl_3$) in 71% yield. Use of the benzylidene protecting group with this substrate is convenient because it effectively selects the C-2 symmetric diol. Reductive cleavage of **2** by treatment with Et_3SiH and the assistance of $TiCl_4$ at −78 °C cleanly provided the monobenzyl ether **3** ($[\alpha]^{27}_D$ = +1.96°, *c* = 1.02, $CHCl_3$) in 88% yield. Exposure of **3** to aqueous CF_3COOH produced the desired lactone carboxylic acid **4** ($[\alpha]^{17}_D$ = −8.51°, *c* = 0.94, EtOH) in 86% yield.

In a more convenient route to the large-scale preparation of **4**, we have utilized the diethyl ester **5** prepared from D-mannitol.[10] Deprotection of the acetonide of **5** followed by reprotection with benzaldehyde dimethyl acetal gave benzylidene diester **6** ($[\alpha]^{25}_D$ = +38.2°, *c* = 1.0, $CHCl_3$) in 85.3% yield. As already described, reduction of **6** with a mixed reagent system of Et_3SiH and $TiCl_4$ afforded monobenzyl ether **7** ($[\alpha]^{26}_D$ = −3.6°, *c* = 1.9, $CHCl_3$) in 97% yield. After selective hydrogenation of the double bond in **7** using 5% Rh/C as a catalyst, hydrolysis of the resultant saturated diester under acidic conditions produced **4** ($[\alpha]^{16}_D$ = −9.80°, *c* = 1.02, EtOH) in 87% yield, as well as minor amounts of the corresponding ethyl ester **8** (5%).[11] Compound **4** prepared by this sequence was identical with the specimen derived from D-tartaric acid (vide supra).[12]

The succeeding decarboxylative halogenation[13] of **4** was found to be rather troublesome, probably due to the presence of the sensitive benzyl ether function. For example, the use of the Kochi reaction ($Pb(OAc)_4$–LiCl)[14] or Hunsdiecker conditions with some modifications (HgO–Br_2)[15] were unsuccessful. After numerous trials with alternative procedures, we finally found that iodosobenzene diacetate in refluxing CCl_4–$CHCl_2CHCl_2$ containing an equimolar amount of iodine[16] is productive, resulting in the formation of the iodide **9** ($[\alpha]^{16}_D$ = +24.4°, *c* = 0.9, $CHCl_3$) in 66% yield as colorless plates, mp 45.5–46.0 °C. The intramolecular alkylation of **9** was accomplished by treatment with 1.2 equiv of $LiN(TMS)_2$ in THF at −90 °C for 1 h to afford the bicyclic lactone **10** ($[\alpha]^{18}_D$ = −55.3°, *c* = 1.5, $CHCl_3$), mp 62.5–63.0 °C, in 94% yield. The stereochemical outcome of this alkylation is undoubtedly the desired cis orientation based on the structural constraints revealed by molecular model. Also, the optical purity was determined to be >99% by HPLC analysis (DAICEL CHIRALCEL OJ; hexane/*i*-PrOH (9:1)). The absolute configuration of **10** was further unambiguously confirmed after conversion to the corresponding free alcohol **11** ($[\alpha]^{23}_D$ = −22.5°, *c* = 2.0, $CHCl_3$ (lit.[7d] $[\alpha]^{23}_D$ = −21.5°, *c* = 2.0, $CHCl_3$)), mp 160.0–162.0 °C (lit.[7d] mp 163.5–165.0 °C), by catalytic debenzylation.

In summary, the cyclohexyl fragment of FK-506 has been constructed from D-tartaric acid and from D-mannitol in optically pure form. The overall yield of **10** is 33% from diol **1** and 45% from diester **5**, and both sequences are six steps. With regard to the former sequence, its synthetic

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(11) Hydrolysis under basic conditions resulted in a rather decreased yield.

(12) The higher optical rotation of the specimen derived from D-mannitol exhibits superiority over the process employing D-tartaric acid. In the latter example we thought that the loss of optical purity has occured at the stage of the preparation of diol **1**, although the reason is not clear.

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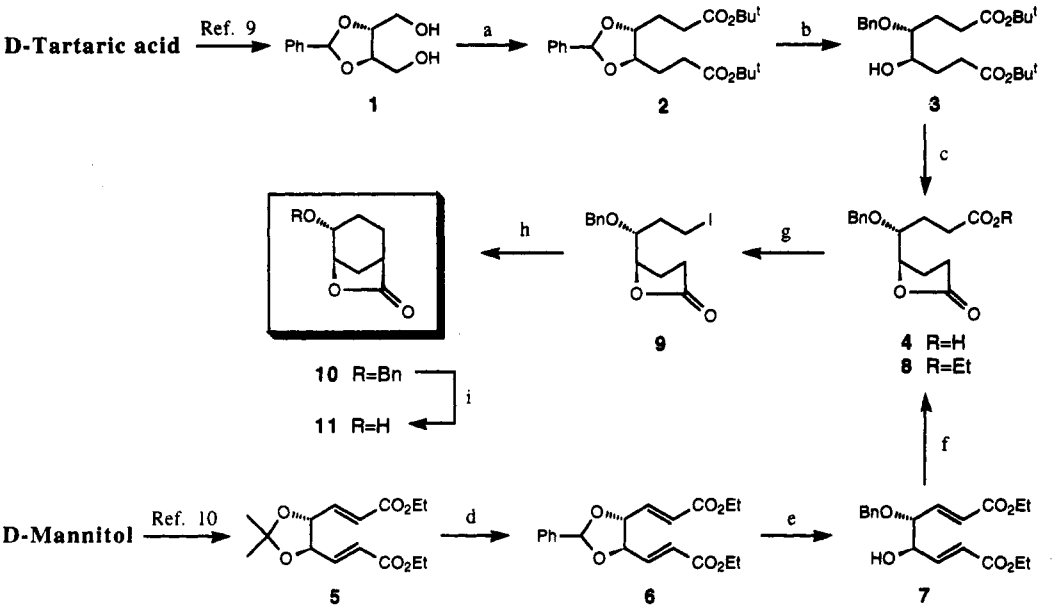
Scheme I[a]



[a] Reagents and conditions: (a) (i) Tf_2O, pyridine, −15 °C, 20 min; (ii) $LiCH_2COO$-*t*-Bu (2.5 equiv), THF–DMPU (6:1), −78 °C, 30 min, 71% overall; (b) Et_3SiH (4 equiv), $TiCl_4$ (1.5 equiv), CH_2Cl_2, −78 °C, 20 min, 88%; (c) CF_3COOH–H_2O (7:3), CH_2Cl_2, rt, 1 h, 86%; (d) (i) 2 M HCl, CH_3CN–H_2O (95:5), 87%; (ii) $PhCH(OMe)_2$, *p*-$TsOH{\cdot}H_2O$ (cat.), C_6H_6, Δ, 98%; (e) Et_3SiH (4 equiv), $TiCl_4$ (1.5 equiv), CH_2Cl_2, −78 °C, 20 min, 97%; (f) (i) H_2, 5% Rh/C, AcOEt, 3 h; (ii) concd HCl, AcOH, rt, 3 h, 87% overall; (g) $PhI(OAc)_2$ (1.06 equiv), I_2 (1.06 equiv), CCl_4–$CHCl_2CHCl_2$ (4:1), reflux, *hν*, 50 min, 66%; (h) $LiN(TMS)_2$ (1.2 equiv), THF, −90 °C, 1 h, 94%; (i) H_2, 10% $Pd(OH)_2$/C, AcOEt, rt, 1.5 h, 100%.

utility is evident since one can easily prepare an antipode of **10** by utilizing L-tartaric acid as the chiral source. Given the described accessibility of **10** and **11** from commercially available simple chiral precursors, our procedure constitutes an expeditious route to the target system.

Experimental Section

General Procedures. All melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 90 and 22.6 MHz unless otherwise noted. HPLC analyses were performed using a UV (λ = 254 nm) detector and DAICEL CHIRALCEL OJ column with hexane/*i*-PrOH as an eluent. TLC was conducted by using Merck precoated Kieselgel 60F-254 plates (0.25 mm). Preparative TLC was carried out on 2-mm-thick Merck Kieselgel 60PF-254. Wakogel C-300 was employed for column chromatography.

All solvents were dried immediately before use. Et_2O, THF, and C_6H_6 were distilled from sodium/benzophenone ketyl; CH_2Cl_2, Et_3N, pyridine, CH_3CN, 2,6-dimethylpropyleneurea (DMPU), *i*-Pr_2NH, and $HN(TMS)_2$ were distilled from CaH_2. CCl_4 and $CHCl_2CHCl_2$ were distilled from P_2O_5. All reactions involving air- or moisture-sensitive materials were carried out under an argon atmosphere.

Di-*tert*-butyl (4*R*,5*R*)-4,5-*O*-Benzylidene-4,5-dihydroxyoctanedioate (2). To a solution of diol **1** (93 mg, 0.44 mmol) and pyridine (0.2 mL) in CH_2Cl_2 (1 mL) at −15 °C was added a solution of Tf_2O (370 mg, 1.31 mmol) in CH_2Cl_2 (0.5 mL), and the mixture was stirred at this temperature for 15 min. The mixture was diluted with CH_2Cl_2, washed with aqueous $CuSO_4$, saturated $NaHCO_3$, and saturated NaCl, and dried (Na_2SO_4). Evaporation of the solvent provided the corresponding ditriflate [R_f = 0.72 (Et_2O)] in an almost pure form, which was azeotropically dried with toluene and used for the next reaction.

To a solution of LDA (1.2 mmol from 170 μL of *i*-Pr_2NH and 0.86 mL of 1.4 M *n*-BuLi) in THF (3 mL) at −78 °C was added CH_3CO_2-*t*-Bu (150 μL, 1.1 mmol), and the mixture was stirred for 30 min. Then to this mixture at −78 °C was added DMPU (850 μL) followed by a solution of the above-obtained ditriflate in THF (2 mL), and the mixture was stirred for 30 min. Then the mixture was quenched with saturated $NaHCO_3$, evaporated, and extracted with Et_2O. The extracts were washed with saturated NaCl, dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by silica gel column chromatography (hexane/AcOEt (2:1)) to afford **2** (126 mg, 71%) as a colorless oil: R_f = 0.44 (hexane/AcOEt (2:1)); $[\alpha]^{20}_D$ +25.4° (*c* 1.0, $CHCl_3$); FTIR (neat) 1729, 1369, 1154, 1096, 1069, 849, 758, 698 cm^{-1}; ^1H NMR δ 1.43 (18 H, s), 1.6–2.1 (4 H, m), 2.44 (4 H, m), 3.81 (2 H, m), 5.85 (1 H, s), 7.37 (5 H, m); ^{13}C NMR δ 28.16 (×6), 31.84 (×2), 32.00 (×2), 80.32 (×2), 81.54 (×2), 102.76, 126.55 (×2), 128.19 (×2), 129.11, 137.95, 172.10, 172.16; MS *m/z* (rel intensity) 406 (M^+, 1.4), 349 (1.1), 333 (1.7), 293 (88), 277 (56), 244 (19), 217 (9), 188 (93), 171 (100), 153 (28), 107 (71), 105 (86), 91 (10), 85 (37), 57 (72), 41 (19); HRMS calcd for $C_{23}H_{34}O_6$ 406.2355, found 406.2357.

Di-*tert*-butyl (4*R*,5*R*)-4-(Benzyloxy)-5-hydroxyoctanedioate (3). To a solution of **2** (216 mg, 0.53 mmol) and Et_3SiH (340 μL, 2.13 mmol) in CH_2Cl_2 (7 mL) was added $TiCl_4$ (0.9 M in CH_2Cl_2; 890 μL, 0.80 mmol) at −78 °C, and the resulting yellow solution was stirred at this temperature for 20 min. The mixture was quenched with H_2O and extracted with AcOEt. The extracts were dried (Na_2SO_4) and concentrated. The crude product was purified by silica gel column chromatography (petroleum ether/acetone (9:1)) to afford **3** (190 mg, 88%) as a colorless oil: R_f = 0.32 (petroleum ether/acetone (6:1)); $[\alpha]^{27}_D$ +1.96° (*c* 1.02, $CHCl_3$); FTIR (neat) 3468, 1728, 1368, 1154, 1073, 849, 737, 698 cm^{-1}; ^1H NMR δ 1.44 (18 H, s), 1.5–2.0 (4 H, m), 2.0–2.5 (5 H, m), 3.2–3.7 (2 H, m), 4.53 and 4.65 (2 H, ABq, J_{AB} = 11.4 Hz), 7.32 (5 H, s); ^{13}C NMR δ 25.38, 28.03 (×6), 28.43, 31.02, 31.94, 71.85, 72.55, 80.11, 80.17, 80.99, 127.58, 127.70 (×2), 128.25 (×2), 138.01, 172.56, 172.98; MS *m/z* (rel intensity) 409 (M^+ + 1, 0.5), 387 (0.6), 352 (1.1), 296 (13), 279 (36), 249 (8), 223 (3), 193 (90), 171 (21), 159 (21), 136 (6), 103 (52), 91 (100), 85 (31), 65 (6), 57 (49), 41 (10); HRMS calcd for $C_{23}H_{36}O_6$ + H 409.2590, found 409.2577.

Diethyl (4*R*,5*R*)-4,5-*O*-Benzylidene-4,5-dihydroxy-2,6-octadienedioate (6). To an ice-cooled solution of **5** (3.0 g, 10.1 mmol) in 95% aqueous CH_3CN (10 mL) was added dropwise 2 M HCl (2 mL), and the mixture was stirred at rt overnight. After removal of the solvent, the residual solid was recrystallized from Et_2O/hexane to afford the corresponding diol (2.27 g, 87%) as colorless needles: mp 59.5–61.0 °C; R_f = 0.25 (hexane/AcOEt (1:1)); $[\alpha]^{28}_D$ +63.2° (*c* 1.06, $CHCl_3$).

A solution of the above-obtained diol (1.50 g, 5.8 mmol) and $PhCH(OMe)_2$ (1.3 g, 5.04 mmol) in C_6H_6 (5 mL)[17] containing

p-TsOH·H_2O (3 mg) was carefully heated until the C_6H_6/MeOH azeotrope (57 °C) began to distill. Heating was continued over about 1 h during which time the temperature of the distillate had risen to 72 °C. The mixture was allowed to cool to rt, and additional C_6H_6 (3 mL) and *p*-TsOH·H_2O (catalytic amount) were introduced, and the mixture was stirred at reflux overnight. After removal of the C_6H_6/MeOH azeotrope, the mixture was further refluxed for 1.5 h. Then the mixture was diluted with CH_2Cl_2 and neutralized with K_2CO_3 powder. After removal of the insoluble substance by filtration through Celite, the solvent was evaporated. The crude product was purified by silica gel column chromatography (petroleum ether/acetone (2:1)) to afford **6** (1.98 g, 98%) as a colorless oil: R_f = 0.53 (hexane/acetone (2:1)); $[\alpha]^{25}_D$ +38.2° (*c* 1.0, $CHCl_3$); FTIR (neat) 1721, 1663, 1302, 1275, 1179, 1028, 980, 762, 698 cm^{-1}; ^1H NMR δ 1.30 (3 H, t, *J* = 7.0 Hz), 1.31 (3 H, t, *J* = 7.0 Hz), 4.22 (2 H, q, *J* = 7.0 Hz), 4.23 (2 H, q, *J* = 7.0 Hz), 4.47 (2 H, m), 6.08 (1 H, s), 6.19 (2 H, dd, *J* = 15.5, 0.8 Hz), 6.95 (2 H, ddm, *J* = 15.5, 4.2 Hz), 7.2–7.6 (5 H, m); ^{13}C NMR δ 14.22, 60.75, 79.74, 81.06, 104.56, 123.56, 124.05, 126.42 (×2), 128.34 (×2), 129.53, 136.73, 140.88, 141.82, 165.33, 165.42; MS *m/z* (rel intensity) 346 (M^+, 1.4), 345 (M^+ − 1, 5.2), 218 (6.4), 195 (7.1), 173 (11), 145 (22), 112 (100), 105 (26), 84 (51), 77 (8.4), 55 (3.2), 39 (4.6); HRMS calcd for $C_{19}H_{22}O_6$ 346.1416, found 346.1391.

Diethyl (4*R*,5*R*)-4-(Benzyloxy)-5-hydroxy-2,6-octadienoate (7). To a solution of **6** (5.0 g, 14.4 mmol) and Et_3SiH (9.3 mL, 58.2 mmol) in CH_2Cl_2 (120 mL) at −78 °C was added $TiCl_4$ (1 M in CH_2Cl_2; 22 mL, 22 mmol), and the resulting yellow solution was stirred at this temperature for 20 min. The mixture was quenched with H_2O and extracted with AcOEt. The extracts were dried (Na_2SO_4) and evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt (4:1)) to afford **7** (4.88 g, 97%) as a colorless oil: R_f = 0.30 (hexane/acetone (2:1)); $[\alpha]^{26}_D$ −3.6° (*c* 1.9, $CHCl_3$); FTIR (neat) 3470, 1719, 1659, 1306, 1275, 1179, 1105, 1038, 982, 754, 700 cm^{-1}; ^1H NMR δ 1.28 (3 H, t, *J* = 7.0 Hz), 1.30 (3 H, t, *J* = 7.3 Hz), 2.95 (1 H, br d, *J* = 4.4 Hz), 3.8–4.3 (2 H, m), 4.19 (2 H, q, *J* = 7.3 Hz), 4.22 (2 H, q, *J* = 7.0 Hz), 4.39 and 4.65 (2 H, ABq, J_{AB} = 11.6 Hz), 6.08 (1 H, dd, *J* = 15.8, 1.1 Hz), 6.13 (1 H, dd, *J* = 15.6, 1.8 Hz), 6.82 (1 H, dd, *J* = 15.6, 2.1 Hz), 6.88 (1 H, d, *J* = 15.8 Hz), 7.32 (5 H, s); ^{13}C NMR δ 14.13, 60.38, 60.66, 71.54, 72.61, 80.60, 122.61, 125.08, 127.80 (×2), 127.95, 128.38 (×2), 136.88, 142.92, 144.60, 165.36, 165.88; MS *m/z* (rel intensity) 349 (M^+ +1, 0.17), 318 (0.09), 289 (0.14), 257 (0.88), 220 (12), 219 (8.7), 129 (42), 101 (7.2), 92 (24), 91 (100), 83 (8.1), 77 (2.4), 65 (4.3), 55 (2.2); HRMS calcd for $C_{19}H_{24}O_6$ 348.1573, found 348.1583.

(4*R*,5*R*)-5-(Benzyloxy)-7-carboxy-4-heptanolide (4). Method A (from 3). A solution of **3** (106 mg, 0.26 mmol) and 70% aqueous CF_3COOH (0.45 mL) in CH_2Cl_2 (1 mL) was stirred at rt for 1 h. After evaporation of the solvent in vacuo, the residue was purified by preparative TLC ($CHCl_3$/MeOH (19:1)) to afford **4** (62 mg, 86%) as a colorless oil: R_f = 0.46 (AcOEt); $[\alpha]^{17}_D$ −8.51° (*c* 0.94, EtOH); FTIR (neat) 3600–2800, 1771, 1734, 1713, 1186, 1100, 1067, 1026, 743, 700 cm^{-1}; ^1H NMR δ 1.7–2.7 (8 H, m), 3.54 (1 H, dt, *J* = 6.8, 5.6 Hz), 4.53 (1 H, dt, *J* = 6.6, 5.3 Hz), 4.65 (2 H, s), 7.32 (5 H, s); ^{13}C NMR δ 24.28, 24.98, 28.28, 29.50, 72.98, 79.01, 82.06, 127.70, 127.80 (×2), 128.28 (×2), 137.64, 177.04, 178.38; MS *m/z* (rel intensity) 278 (M^+, 1.4), 260 (5.3), 193 (12), 172 (12), 154 (11), 136 (15), 126 (7), 107 (8), 91 (100), 85 (61), 77 (2.2), 65 (8), 57 (3); HRMS calcd for $C_{15}H_{18}O_5$ 278.1154, found 278.1178.

Method B (from 7). A mixture of **7** (1.08 g, 3.1 mmol) and 5% Rh–C (80 mg) in AcOEt (10 mL) was stirred under H_2 at rt for 3 h. After removal of the catalyst by filtration through Celite, the solvent was evaporated in vacuo. The residue was dissolved in AcOH (5 mL) and concd HCl (2.5 mL), and the mixture was stirred at rt for 3 h. Evaporation of the solvent gave a crude product which was purified by silica gel column chromatography (AcOEt) to afford **4** (730 mg, 87%) as a colorless oil along with the corresponding ethyl ester **8** (50 mg, 5%). For **4**: R_f = 0.46 (AcOEt); $[\alpha]^{16}_D$ −9.80° (*c* 1.02, EtOH); spectral data were identical with the specimen obtained from **3**. For (4*R*,5*R*)-5-(benzyloxy)-7-(ethoxycarbonyl)-4-heptanolide (**8**): R_f = 0.34 (hexane/acetone (2:1)); $[\alpha]^{22}_D$ −8.38° (*c* 1.6, $CHCl_3$); FTIR (neat) 1777, 1732, 1181, 1100, 1028, 743, 700 cm^{-1}; ^1H NMR δ 1.24 (3 H, t, *J* = 7.0 Hz), 1.6–2.7 (8 H, m), 3.52 (1 H, ddd, *J* = 12.3, 7.3, 1.5 Hz), 4.11 (2 H, q, *J* = 7.0 Hz), 4.52 (1 H, m), 4.61 and 4.69 (2 H, ABq, J_{AB} = 11.7 Hz), 7.32 (5 H, s); ^{13}C NMR δ 14.10, 24.31, 25.20, 28.19, 29.65, 60.26, 72.85, 79.20, 81.94, 127.58, 127.70 (×2), 128.19 (×2), 137.77, 172.80, 176.64; MS *m/z* (rel intensity) 307 (M^+ + 1, 0.5), 306 (M^+, 0.2), 260 (0.7), 235 (1.3), 221 (11), 200 (20), 182 (5), 154 (4.2), 136 (22), 129 (9), 105 (8), 91 (100), 85 (36), 65 (6), 57 (7); HRMS calcd for $C_{17}H_{22}O_5$ 306.1469, found 306.1469.

(4*R*,5*R*)-5-(Benzyloxy)-7-iodo-4-heptanolide (9). A solution of **4** (1.38 g, 4.96 mmol) in CCl_4 (85 mL) and $CHCl_2CHCl_2$ (20 mL)[18] containing $PhI(OAc)_2$ (850 mg, 2.64 mmol) and I_2 (670 mg, 2.64 mmol) was irradiated with 500-W tungsten lamp for 20 min at reflux. Then another portion of $PhI(OAc)_2$ (850 mg) and I_2 (670 mg) were added, and the irradiation at this temperature was continued for 30 min. The mixture was diluted with CH_2Cl_2, washed with aqueous $Na_2S_2O_3$ and saturated NaCl, and dried ($MgSO_4$). Evaporation of the solvent gave a crude product which was purified by silica gel column chromatography (Et_2O) to afford iodide **9** (1.18 g, 66%): colorless plates from hexane–Et_2O; mp 45.5–46.0 °C; R_f = 0.46 (Et_2O); $[\alpha]^{16}_D$ +24.4° (*c* 0.9, $CHCl_3$); FTIR (KBr) 1777, 1181, 1142, 1100, 1061, 912, 752, 698 cm^{-1}; ^1H NMR (400 MHz) δ 1.9–2.15 (3 H, m), 2.2–2.3 (1 H, m), 2.48 (1 H, ddd, *J* = 17.6, 9.8, 8.3 Hz), 2.57 (1 H, ddd, *J* = 17.6, 9.8, 5.6 Hz), 3.29 (2 H, dd, *J* = 7.3, 6.4 Hz), 3.65 (1 H, dt, *J* = 7.8, 4.8 Hz), 4.56 (1 H, dt, *J* = 7.3, 4.8 Hz), 4.69 and 4.75 (2 H, ABq, J_{AB} = 11.5 Hz), 7.35 (5 H, s); ^{13}C NMR δ 1.96, 24.10, 28.09, 34.16, 73.34, 80.02, 81.24, 127.67 (×2), 128.22 (×2), 137.55, 176.46; MS *m/z* (rel intensity) 360 (M^+, 3.1), 275 (12), 254 (2.6), 233 (11), 176 (26), 148 (1.8), 127 (23), 107 (5.2), 91 (100), 85 (72), 65 (6.9), 57 (2.9), 41 (2). Anal. Calcd for $C_{14}H_{17}IO_3$: C, 46.68; H, 4.76. Found: C, 46.75; H, 4.82.

(1*R*,4*R*,5*R*)-4-(Benzyloxy)-6-oxabicyclo[3.2.1]octan-7-one (10). To a solution of **9** (330 mg, 0.92 mmol) in THF (10 mL) at −90 °C was added a solution of $LiN(TMS)_2$ (1.1 mmol from 230 μL of $HN(TMS)_2$ and 0.54 mL of 1.69 M *n*-BuLi) in THF (3 mL), and the mixture was stirred at this temperature for 1 h. The mixture was quenched with 2 M HCl, concentrated, and extracted with AcOEt. The extracts were washed with aqueous $Na_2S_2O_3$ and saturated NaCl, dried ($MgSO_4$), and concentrated. The crude product was purified by preparative TLC (hexane/AcOEt (2:1)) to afford **10** (200 mg, 94%): colorless plates from hexane–Et_2O; mp 62.5–63.0 °C; R_f = 0.66 (Et_2O); $[\alpha]^{18}_D$ −55.3° (*c* 1.5, $CHCl_3$); FTIR (KBr) 1794, 1154, 1082, 910 cm^{-1}; ^1H NMR (400 MHz) δ 1.7–1.9 (3 H, m), 1.97 (1 H, m), 2.21 (1 H, dt, *J* = 11.7, 5.9 Hz), 2.39 (1 H, d, *J* = 11.7 Hz), 2.59 (1 H, m), 3.83 (1 H, br s), 4.49 and 4.61 (2 H, ABq, J_{AB} = 11.7 Hz), 4.70 (1 H, t, *J* = 5.4 Hz), 7.33 (5 H, m); ^{13}C NMR δ 23.03, 23.73, 31.69, 38.22, 71.51, 72.30, 77.70, 127.40 (×2), 127.80, 128.44 (×2), 138.01, 178.44; MS *m/z* (rel intensity) 232 (M^+, 5.4), 214 (4.3), 204 (3.3), 176 (6.6), 141 (41), 126 (12), 123 (24), 113 (26), 107 (26), 97 (25), 91 (100), 85 (15), 67 (27), 65 (15), 57 (4.7), 41 (11). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.48; H, 6.93.

(1*R*,4*R*,5*R*)-4-Hydroxy-6-oxabicyclo[3.2.1]octan-7-one (11). Benzyl ether **10** (100 mg, 0.43 mmol) was hydrogenatd in AcOEt (2 mL) with 10% $Pd(OH)_2$/C (10 mg) as a catalyst at rt for 1.5 h. The mixture was filtered through Celite and rinsed thoroughly with AcOEt. Evaporation of the solvent gave almost pure **11** (62 mg, 100%): colorless needles from CH_2Cl_2–hexane; mp 160.0–162.0 °C (lit.[7d] mp 163.5–165.0 °C); R_f = 0.27 (Et_2O); $[\alpha]^{23}_D$ −22.5° (*c* 2.0, $CHCl_3$) [lit.[7d] $[\alpha]^{23}_D$ −21.5° (*c* 2.0, $CHCl_3$)]; FTIR (KBr) 3418, 1753, 1157, 1040, 970, 914, 708 cm^{-1}; ^1H NMR (400 MHz) δ 1.7–2.0 (4 H, m), 2.08 (1 H, m), 2.17–2.23 (1 H, m), 2.39 (1 H, d, *J* = 12.2 Hz), 2.60 (1 H, m), 4.18 (1 H, br s), 4.66 (1 H, t, *J* = 5.4 Hz); ^{13}C NMR δ 22.61, 26.94, 31.02, 38.46, 64.56, 79.41, 179.32; MS *m/z* (rel intensity) 143 (M^+ + 1, 9.2), 142 (M^+, 26), 124 (100), 114 (18), 100 (40), 96 (21), 86 (28), 82 (31), 71 (47), 70 (67), 57 (24), 44 (54). Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.50; H, 7.18.

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(17) C_6H_6 can be replaced with toluene.

(18) The reaction should be proceeded in $CHCl_2CHCl_2$ as a sole solvent, although we did not check the reaction conditions furthermore.

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Supplementary Material Available: ^{1}H NMR spectra of 2-4 and 6-10 (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Shape-Selective Synthesis of 2,6-Dicyclohexylnaphthalene over HY Zeolites

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As precursors of 2,6-naphthalenedicarboxylic acid, 2,6-dialkylnaphthalenes are potential starting materials in the production of polyester fibers and plastics with superior properties[1,2] and of thermotropic liquid crystal polymers.[3] The interest of such derivatives is shown by the increasing number of recent patents relevant to their preparation and separation.[3-5] However, the selective formation of 2,6-dialkylnaphthalenes in the alkylation of naphthalene is not obvious, not only with conventional Friedel-Crafts catalysts[6-8] but also over solid catalysts such as silica/alumina[9-11] or zeolites. The latter, which are well-known as shape-selective catalysts for acylation and alkylation of aromatic derivatives,[12,13] have been used in the gas-phase methylation of naphthalene with methanol[14,15] and more recently in the liquid-phase isopropylation of naphthalene with isopropyl bromide[16] or propene.[3,17] It was found that alkylation of naphthalene could be carried out efficiently over such zeolite catalysts with a good selectivity for the formation of 2-alkylnaphthalene and 2,6-/2,7-dialkylnaphthalenes. Unfortunately, the selective formation of the 2,6 isomer was not possible in any case, whatever zeolites and alkylating agents were used.

Such a selectivity might be found with more hindered alkylating agents, such as cyclohexyl derivatives. Our interest[16] in the shape-selective synthesis of a 2,6-dialkylnaphthalene over zeolites was stimulated by the finding that, in the cyclohexylation reaction of naphthalene over aluminum chloride, the 2,6-dicyclohexylnaphthalene was isolated from the reaction mixture by crystallization.[18,19]

We have used the combination of such a property of the 2,6-dicyclohexylnaphthalene with the potential shape-selectivity properties of zeolites in the study of the cyclohexylation reaction of naphthalene with cyclohexyl bromide and cyclohexene over protonic zeolites.

The present paper is concerned with the results obtained, leading to the selective synthesis of 2,6-dicyclohexylnaphthalene, which is known, on the other hand, to yield 2,6-naphthalenedicarboxylic acid by oxidation under the same conditions as those described for other 2,6-dialkylnaphthalenes.[20]

The catalytic activities of a sample of H-mordenite and two samples of HY zeolites were studied in the cyclohexylation reaction of naphthalene at 80 °C and 200 °C, respectively (Table I).

The H-mordenite presents a weak activity in the reaction with cyclohexyl bromide, as shown by the low conversion of naphthalene (6%) at 200 °C, whereas the HY zeolites appear to be very efficient even at lower temperature. The ultrastable zeolite HY (Si/Al ratio = 2.5) and the dealuminated sample (Si/Al ratio = 20) exhibit a similar activity (high conversion ($\simeq$95%) after a 10-min reaction with cyclohexyl bromide at 200 °C) and similar selectivities at the same temperatures.

When cyclohexene is used as the alkylating agent instead of cyclohexyl bromide, a slight difference is observed if the reaction is carried out in the same conditions (naphthalene and alkylating agent put together in the autoclave). When cyclohexene is added drop by drop (run 8) to the stirred mixture, the same results are then obtained, both in conversion and selectivity.

It can be seen, from Table I, that at lower temperature, the main products are monosubstituted derivatives, which consist of a mixture of 1-cyclohexyl- and 2-cyclohexylnaphthalenes. When the temperature is increased, the amount of dicyclohexyl derivatives increases drastically. These compounds are mainly 2,6- and 2,7-dicyclohexylnaphthalenes, formed by consecutive cyclohexylation of the monosubstituted 2-cyclohexylnaphthalene.

This suggests that the α,α and α,β isomers, produced by the cyclohexylation of the 1-cyclohexyl derivative, cannot be formed inside or cannot diffuse through the pores of the Y zeolite because of their steric hindrance. That is not the case for the 2,6- and 2,7-dicyclohexyl derivatives (β,β isomers) for which the pores of the zeolite are large enough to allow their formation and diffusion.

Moreover, the thermodynamic effect favors the β isomer at high temperature as for isopropylnaphthalene derivatives (equilibrium $\alpha \rightleftharpoons \beta$ 1.5-98.5)[8] or *tert*-butylnaphthalene derivatives,[21] and consequently, in a second consecutive step, the formation of β,β-disubstituted isomers.

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