Synthetic Study on 1,3-Polyols. Stereoselective Synthesis of Four Diastereoisomers of 1,2,4,6,8-Pentol Derivatives

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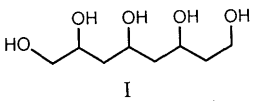
The stereoselective synthesis of four diastereoisomers of octane-1,2,4,6,8-pentol derivatives is described by means of a convergent 1,3-polyol synthesis using a four-carbon unit, where 1,3-*syn*- and *anti*-selective reductions have been effectively employed.

Keywords 1,3-polyol synthesis; 1,3-diastereoselective reduction; octane-1,2,4,6,8-pentol derivative; 1,2,4,6-tetrabenzoyloxy-7-octene; lithium aluminum hydride; diethylmethoxyborane; tetramethylammonium triacetoxyborohydride

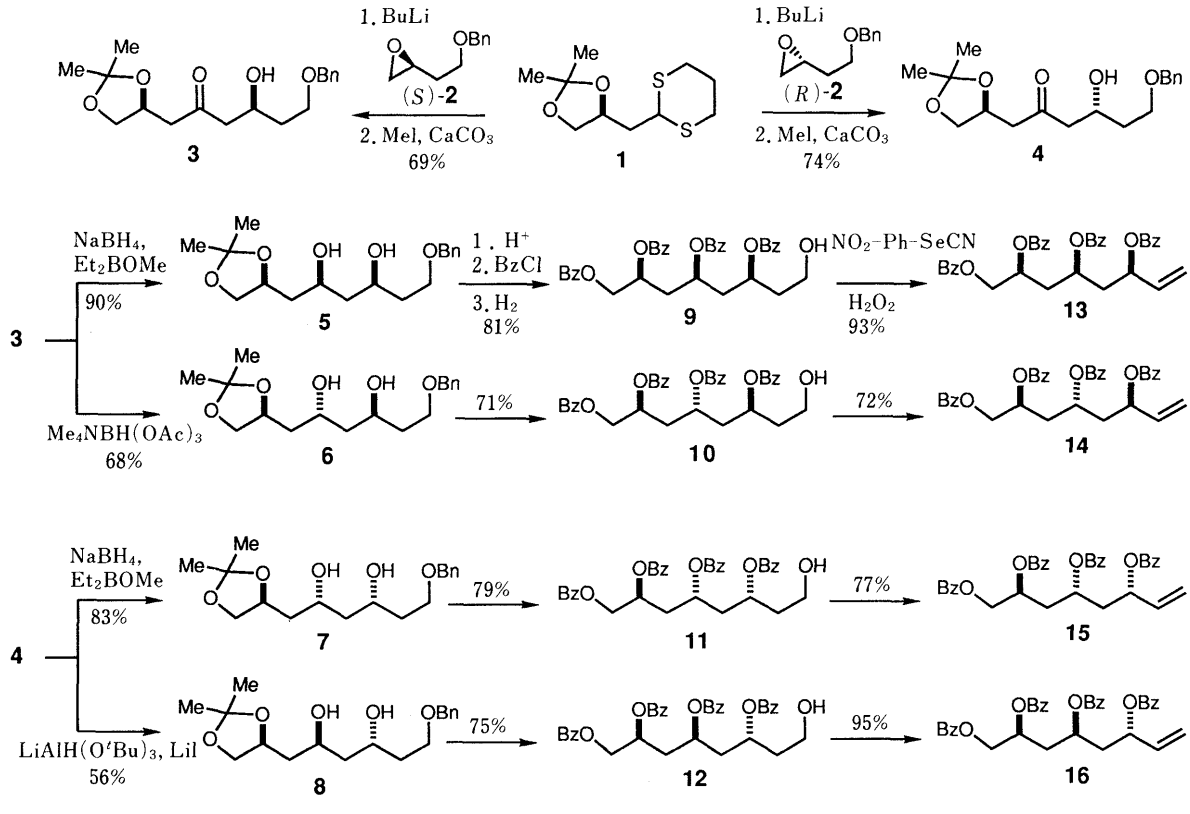
Synthesis of 1,3-polyols in a stereocontrolled manner is of considerable current interest, since *syn*- and *anti*-diols are recurring units of various polyacetate-derived natural products, such as polyene macrolide antibiotics,[1] and convergent strategies to prepare an alternating polyol chain have recently been developed.[2] On the other hand, determination of stereochemistry in acyclic polyol chains remains a difficult task. Conventional methods[3] for assigning the absolute configuration require circular dichroic (CD) spectroscopic analysis and partial synthesis of degradation products after determination of relative stereochemistry by ^{1}H-nuclear magnetic resonance (^{1}H-NMR) analysis. In these stereochemical studies, the CD method was used for molecules with a rigid ring.[3a,b] Application of the method to acyclic 1,3-polyols is limited to simple diols[4] because of conformational flexibility. Therefore, it is important to develop a new method for determining the absolute stereochemistry. For this purpose, we required 1,3-polyols whose absolute stereochemistry was established. In this paper, we present efficient syntheses of four diastereoisomers of 1,2,4,6,8-pentol I for CD analysis.



I

Chart 1

The general strategy for the construction of the stereoisomers was based on a polyol chain synthesis using a four-carbon unit **1**.[5] The optically pure epoxide (*S*)-**2** and its enantiomer (*R*)-**2** were prepared from (*S*)-(−)-butane-1,2,4-triol (98% ee).[6] The coupling of a lithiodithiane, prepared by treatment of **1** with *n*-butyllithium at −30 °C for 2 h, with (*S*)- and (*R*)-**2** gave the adducts, dedithio-



'Bu = *tert*-butyl

Chart 2

ketalization of which was effected with MeI–$CaCO_3$ in aqueous acetonitrile[7] to give the hydroxy ketones **3** and **4**, respectively, in good yield.

The reduction of the carbonyl groups of **3** and **4** is a crucial step to obtain stereochemically homogeneous diastereomers in the present synthesis. The relative stereochemistry of C-4 hydroxy centers can be established by the selection of appropriate *syn*- and *anti*-selective reducing agents. Reduction of **3** utilizing the *syn*-selective reduction that we have developed earlier[5a] ($LiAlH_4$–LiI) gave the *syn*-diol **5** in 85% yield. The diastereoselectivity of the reduction (*syn*:*anti*=94:6) was determined by the intensity of ^{1}H-NMR signals of the corresponding acetonide methyl groups in benzene-d_6 (*syn*, 1.35 ppm; *anti*, 1.42 ppm). Reduction of **3** with Et_2BOMe–$NaBH_4$[8] according to the procedure of Prasad and co-workers afforded a 97:3 mixture of *syn*- and *anti*-diols, from which **5** was isolated in 90% yield.

Alternatively, the reduction of **3** with $Me_4NBH(OAc)_3$[2e] provided the *anti*-diol **6** in 68% yield. The selectivity of this reduction is *anti*:*syn*=87:13. The *syn*-diol is less polar than the *anti*-diol and both were separated by careful flash chromatography on silica gel. The stereochemical outcome of the *syn*- and *anti*-selective reductions was confirmed by the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) chemical shift correlations of the acetonides derived from the diols **5** and **6** developed by Rychnovsky *et al.*[9]

On the other hand, the *syn*-1,3-diol stereochemical relationship in **7** was established by reduction of **4** with Et_2BOMe–$NaBH_4$ to afford a 99:1 mixture of **7** and **8**. The *syn*-diol **7** was isolated in 83% yield. Moreover, treatment of **4** with $LiAlH(O^tBu)_3$–LiI[5c] provided the complementary *anti*-diol **8** in 56% yield after chromatographic separation of the 7:93 mixture. The observed diastereoselection for both transformations and the relative stereochemistry of **7** and **8** were determined by ^{1}H- and ^{13}C-NMR analyses, respectively, as described above.

We next turned our attention to the derivatization of **5**—**8** for CD spectroscopic analysis. Treatment of **5**—**8** with acid followed by perbenzoylation and hydrogenolysis of the benzyl group afforded the hydroxy benzoates **9**—**12**, respectively, in good yield. Finally, the terminal hydroxy group of **9**—**12** was dehydrated by reaction with *o*-nitrophenyl selenocyanate in the presence of tri-*n*-butylphosphine[10] followed by H_2O_2 to yield four diastereomeric allylic benzoates **13**—**16**.

Compounds **9**—**16** have benzoate groups as a chromophore and are appropriate for CD analysis. Application of the CD exciton chirality method to the stereochemically defined hydroxy benzoates and allylic benzoates will be reported in due course.[11]

Experimental

Optical rotations were measured on a JASCO DIP-370 digital polarimeter. Infrared (IR) spectra were taken on a Hitachi 215 spectrometer. ^{1}H-NMR spectra were measured on JEOL GX-400 and 270 spectrometers; chemical shifts are given in ppm with tetramethylsilane as an internal standard. Mass spectra (MS) were taken on Shimadzu GCMS QP-1000 and JEOL HX-110 mass spectrometers. Flash chromatography was performed with Silica gel 60 (230—400 mesh).

(2*S*,6*S*)-8-(*O*-Benzyl)-1,2-(*O*-isopropylidene)octan-4-oxo-1,2,6,8-tetrol (3) A stirred solution of **1** (732 mg, 3.13 mmol) in dry tetrahydrofuran (THF) (7 ml) under nitrogen at −40 °C was treated with 1.6 M *n*-butyllithium in hexane (3.25 ml). The solution was stirred at −30 °C for 2 h and then a solution of (*S*)-**2** (508 mg, 2.86 mmol) in dry THF (3 ml) was added. The reaction vessel was closed under positive pressure of nitrogen and stored at −20 °C for 42 h. The reaction was quenched with aqueous NH_4Cl and the mixture was extracted with ethyl acetate (EtOAc). The extract was washed with water and brine, dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography (20% EtOAc–hexane) gave an adduct (918 mg, 78%) as a colorless oil. A mixture of the adduct (902 mg, 2.18 mmol), $CaCO_3$ (2.2 g, 21.8 mmol), and MeI (13 ml) in 80% aqueous acetonitrile (MeCN) (90 ml) was stirred at room temperature for 23 h. The mixture was filtered through a short column of Celite using EtOAc. The filtrate was concentrated to dryness and the residue was purified by flash chromatography (40% EtOAc–hexane) to give **3** (623 mg, 89%) as a colorless oil, $[\alpha]_D^{25}$ +16.4° (*c*=0.91, $CHCl_3$). IR ($CHCl_3$): 3500, 1710, 1380, 1370, 1205, 1090 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.34 (3H, s), 1.40 (3H, s), 1.77 (2H, m), 2.62 (3H, m), 2.90 (1H, dd, *J*=16.8, 6.4 Hz), 3.34 (1H, br, OH), 3.54 (1H, dd, *J*=8.4, 6.7 Hz), 3.66 (2H, m), 4.17 (1H, dd, *J*=8.4, 5.1 Hz), 4.27 (1H, m), 4.46 (1H, quintet, *J*=6.7 Hz), 4.51 (2H, s), 7.33 (5H). High resolution electron impact MS (HREIMS) *m/z*: Calcd for $C_{18}H_{26}O_5$: 322.1779. Found: 322.1753.

(2*S*,6*R*)-8-(*O*-Benzyl)-1,2-(*O*-isopropylidene)octan-4-oxo-1,2,6,8-tetrol (4) Coupling reaction of **1** (721 mg, 3.08 mmol) and (*R*)-**2** (500 mg, 2.18 mmol) followed by dedithioketalization was carried out in the same way as for **3** to give **4** (669 mg, 74%) as a colorless oil, $[\alpha]_D^{25}$ −10.0° (*c*=1.0, $CHCl_3$). IR ($CHCl_3$): 3500, 1710, 1450, 1380, 1220, 1100 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.34 (3H, s), 1.40 (3H, s), 1.77 (2H, m), 2.63 (3H, m), 2.90 (1H, dd, *J*=16.5, 6.4 Hz), 3.32 (1H, br, OH), 3.54 (1H, dd, *J*=8.4, 7.1 Hz), 3.65 (2H, m), 4.16 (1H, dd, *J*=8.1, 6.1 Hz), 4.28 (1H, m), 4.46 (1H, quintet, *J*=6.4 Hz), 4.51 (2H, s), 7.32 (5H). HREIMS *m/z*: Calcd for $C_{18}H_{26}O_5$: 322.1779. Found: 322.1784.

(2*S*,4*S*,6*S*)-8-(Benzyloxy)-1,2-(isopropylidenedioxy)octane-4,6-diol (5) A solution of **3** (230 mg, 0.714 mmol) in dry THF (5.5 ml) and dry methanol (MeOH) (1.5 ml) was cooled to −78 °C for 15 min, and then $NaBH_4$ (54 mg, 1.43 mmol) was added in one portion. The mixture was stirred at −78 °C for 2 h, then the reaction was quenched with water, and the whole was extracted with EtOAc. The extract was washed with water and brine, dried ($MgSO_4$), and concentrated to dryness. The residue was dissolved in 30 ml of MeOH and the solvent was evaporated. This procedure was repeated several times. The oil obtained was purified by flash chromatography (5% acetone–CH_2Cl_2) to afford **5** (209 mg, 90%) as a colorless oil, $[\alpha]_D^{25}$ +9.80° (*c*=0.64, $CHCl_3$). IR ($CHCl_3$): 3480, 1600, 1425, 1380, 1370, 1220, 1095 cm^{-1}. ^{1}H-NMR (C_6D_6) δ: 1.22 (2H, m), 1.27 (3H, s), 1.35 (3H, s), 1.50—1.64 (3H), 1.76 (1H, m), 3.36 (1H, dd, *J*=8.1, 7.4 Hz), 3.43 (1H, ddd, *J*=9.4, 7.4, 5.0 Hz), 3.53 (1H, ddd, *J*=9.4, 6.4, 5.0 Hz), 3.80 (1H, br, OH), 3.81 (1H, dd, *J*=8.1, 6.1 Hz), 3.85 (1H, br, OH), 3.90 (1H, m), 4.02 (1H, m), 4.05 (1H, m), 4.26 (2H, s), 7.13—7.23 (5H). HREIMS *m/z*: Calcd for $C_{18}H_{28}O_5$: 324.1935. Found: 324.1973.

(2*S*,4*R*,6*S*)-8-(Benzyloxy)-1,2-(isopropylidenedioxy)octane-4,6-diol (6) A solution of $Me_4NBH(OAc)_3$ (3.0 g, 11.5 mmol) in dry MeCN (0.5 ml) and anhydrous acetic acid (0.5 ml) was stirred at room temperature for 30 min and then cooled to −40 °C. To this stirred solution was added a solution of **3** (370 mg, 1.15 mmol) in dry MeCN (1 ml), and the mixture was stirred at −20 °C for 13 h. The reaction was quenched with 28% NH_4OH and extracted with EtOAc. The extract was washed with water and brine, dried ($MgSO_4$), and concentrated *in vacuo*. Purification by flash chromatography (5% acetone–CH_2Cl_2) gave **6** (251 mg, 68%) as a colorless oil, $[\alpha]_D^{25}$ +13.8° (*c*=0.33, $CHCl_3$). IR ($CHCl_3$): 3470, 1600, 1420, 1380, 1370, 1210, 1095 cm^{-1}. ^{1}H-NMR (C_6D_6) δ: 1.35 (3H, s), 1.42 (3H, s), 1.39 (1H, m), 1.47 (2H, t, *J*=5.4 Hz), 1.60 (2H, m), 1.71 (1H, m), 3.17 (1H, br, OH), 3.22 (1H, br, OH), 3.33 (2H, m), 3.48 (1H, t, *J*=8.1 Hz), 3.92 (1H, dd, *J*=8.1, 6.1 Hz), 4.05 (1H, m), 4.18 (2H, s), 4.27 (1H, quintet, *J*=6.4 Hz), 7.07—7.20 (5H). HREIMS *m/z*: Calcd for $C_{18}H_{28}O_5$: 324.1935. Found: 324.1956.

(2*S*,4*R*,6*R*)-8-(Benzyloxy)-1,2-(isopropylidenedioxy)octane-4,6-diol (7) The reduction was carried out in the same way as described for **5**, but employing **4** (263 mg), to give **7** (218 mg, 83%) as a colorless oil after purification by flash chromatography (8% acetone–CH_2Cl_2), $[\alpha]_D^{25}$ −12.65° (*c*=1.23, $CHCl_3$). IR ($CHCl_3$): 3470, 1505, 1420, 1380, 1370, 1200, 1090 cm^{-1}. ^{1}H-NMR (C_6D_6) δ: 1.20 (1H, dt, *J*=14.1, 2.4 Hz), 1.36 (3H, s), 1.43 (3H, s), 1.40—1.66 (5H), 3.30 (1H, m), 3.38 (1H, m), 3.51 (1H, t, *J*=8.1 Hz), 3.69 (1H, br, OH), 3.88 (1H, m), 3.94 (1H, br, OH), 3.98 (1H, dd, *J*=8.1, 6.0 Hz), 4.03 (1H, m), 4.19 (2H, s), 4.31 (1H, quintet, *J*=6.0 Hz), 7.08—7.21 (5H). HREIMS *m/z*: Calcd for $C_{18}H_{28}O_5$: 324.1935. Found: 324.1909.

(2*S*,4*S*,6*R*)-8-(Benzyloxy)-1,2-(isopropylidenedioxy)octane-4,6-diol (8) A solution of **4** (334 mg, 1.04 mmol) and LiI (1.38 g, 10.4 mmol) in dry ether (25 ml) was stirred at −78 °C for 5 min and $LiAlH(O^tBu)_3$ (1.32 g, 5.19 mmol) was added in one portion. The reaction mixture was stirred at −78 °C for 1 h, then the reaction was quenched with MeOH followed by 1 N NaOH, and the whole was stirred until the precipitates were aggregated. The ether layer was separated, washed with water and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash chromatography (20% acetone–CH_2Cl_2) to give **8** (189 mg, 56%) as a colorless oil, $[\alpha]_D^{25}$ −5.55° (*c*=0.67, $CHCl_3$). IR ($CHCl_3$): 3500, 1420, 1380, 1370, 1210, 1095 cm^{-1}. ^{1}H-NMR (C_6D_6) δ: 1.20—1.38 (2H), 1.24 (3H, s), 1.32 (3H, s), 1.54 (2H, t, *J*=5.4 Hz), 1.60 (1H, m), 1.82 (1H, m), 3.28 (1H, t, *J*=7.7 Hz), 3.39—3.56 (4H, 2H of 4H are hydroxylic protons), 3.74 (1H, dd, *J*=8.1, 6.1 Hz), 3.96 (1H, m), 4.10 (1H, m), 4.20 (1H, m), 4.25 (2H, s), 7.08—7.25 (5H). HREIMS *m/z*: Calcd for $C_{18}H_{28}O_5$: 324.1935. Found: 324.1948.

Preparation of the Hydroxy Benzoates (9—12) General Procedure: A solution of a diol (0.5 mmol) in MeOH (10 ml) and 5% HCl–MeOH (1.0 ml) was allowed to stand at room temperature for 16 h. After removal of the solvent, the residue was purified by flash chromatography (8% MeOH–EtOAc) to give a product. A stirred solution of the product in pyridine (2.5 ml) was treated with benzoyl chloride (2.5 mmol), and the solution was stirred at room temperature for 3 h. Excess MeOH was added and the mixture was stirred for 15 min. The reaction mixture was then extracted with ether and the extract was washed with water and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash chromatography (15% EtOAc–hexane) to give a tetrabenzoate. The tetrabenzoate was dissolved in EtOAc (3 ml) and hydrogenated in the presence of $Pd(OH)_2$–C (20% weight of the starting material) for 16 h. The mixture was filtered through a short column of Celite and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (40% EtOAc–hexane) to give a hydroxy benzoate as a colorless oil (**9**, 81%; **10**, 71%; **11**, 79%; **12**, 75%).

(2*S*,4*S*,6*S*)-1,2,4,6-Tetrabenzoyloxy-8-octanol (**9**): $[\alpha]_D^{25}$ −0.40° (*c*=1.0, $CHCl_3$). IR ($CHCl_3$): 3450, 1720, 1600, 1450, 1270, 1110 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.80—2.02 (2H, m), 2.16—2.44 (4H, m), 3.60 (2H, m), 4.44 (1H, dd, *J*=11.8, 5.7 Hz), 4.56 (1H, dd, *J*=11.8, 3.7 Hz), 5.51 (2H, m), 5.66 (1H, m), 7.28—7.58 (12H), 7.80—8.00 (8H). Fast atom bombardment MS (FABMS) *m/z*: 611 (MH^+). HRFABMS *m/z*: Calcd for $C_{36}H_{35}O_9$: 611.2279. Found: 611.2252.

(2*S*,4*R*,6*S*)-1,2,4,6-Tetrabenzoyloxy-8-octanol (**10**): $[\alpha]_D^{25}$ −1.03° (*c*=0.48, $CHCl_3$). IR ($CHCl_3$): 3500, 1720, 1600, 1450, 1270, 1110, 1070, 1025 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.88 (1H, m), 1.96 (1H, m), 2.20—2.40 (4H, m), 3.56 (1H, ddd, *J*=11.8, 9.4, 3.7 Hz), 3.67 (1H, dt, *J*=11.8, 4.7 Hz), 4.46 (1H, dd, *J*=12.1, 6.1 Hz), 4.60 (1H, dd, *J*=12.1, 3.7 Hz), 5.47 (2H, m), 5.62 (1H, m), 7.20—7.58 (12H), 7.82—8.00 (8H). FABMS *m/z*: 611 (MH^+).

(2*S*,4*R*,6*R*)-1,2,4,6-Tetrabenzoyloxy-8-octanol (**11**): $[\alpha]_D^{25}$ −40.66° (*c*=0.94, $CHCl_3$). IR ($CHCl_3$): 3500, 1720, 1600, 1450, 1260, 1110, 1070, 1025 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.89 (1H, m), 1.99 (1H, m), 2.11 (1H, ddd, *J*=14.5, 7.1, 4.4 Hz), 2.22 (1H, ddd, *J*=14.8, 8.4, 3.4 Hz), 2.37—2.52 (2H, m), 3.58 (1H, ddd, *J*=11.7, 9.1, 4.0 Hz), 3.68 (1H, dt, *J*=11.7, 5.0 Hz), 4.45 (1H, dd, *J*=11.8, 5.7 Hz), 4.58 (1H, dd, *J*=11.8, 4.0 Hz), 5.50 (2H, m), 5.62 (1H, m), 7.20—7.55 (12H), 7.80—8.00 (8H). FABMS *m/z*: 611 (MH^+).

(2*S*,4*S*,6*R*)-1,2,4,6-Tetrabenzoyloxy-8-octanol (**12**): $[\alpha]_D^{25}$ −43.94° (*c*=0.83, $CHCl_3$). IR ($CHCl_3$): 3500, 1720, 1600, 1445, 1270, 1110, 1070, 1025 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.80—2.04 (2H, m), 2.16—2.28 (2H, m), 2.33 (1H, ddd, *J*=12.4, 9.1, 3.0 Hz), 2.44 (1H, ddd, *J*=14.0, 8.4, 6.4 Hz), 2.52 (1H, br, OH), 3.56 (1H, m), 3.65 (1H, m), 4.50 (1H, dd, *J*=11.8, 5.7 Hz), 4.60 (1H, dd, *J*=11.8, 3.4 Hz), 5.44 (1H, m), 5.52 (1H, m), 5.66 (1H, m), 7.18—7.77 (12H), 7.80—8.00 (8H). FABMS *m/z*: 611 (MH^+).

Preparation of Allylic Benzoates (13—16) General Procedure: A hydroxy benzoate (0.3 mmol) was dissolved in dry THF (2.0 ml), and *o*-nitrophenyl selenocyanate (0.45 mmol) and tri-*n*-butylphosphine (0.45 mmol) were added. The reaction mixture was stirred at room temperature for 2 h, and the solvent was evaporated off. The residue was purified by flash chromatography (20—30% EtOAc–hexane) to give a selenide. A solution of the selenide and 30% H_2O_2 (3 mmol) in THF (3 ml) was stirred at room temperature for 16 h, and extracted with ether. The extract was washed with water and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by flash chromatography (15% EtOAc–hexane) to give an allylic benzoate as a colorless oil (**13**, 93%; **14**, 72%; **15**, 77%; **16**, 95%).

(2*S*,4*S*,6*R*)-1,2,4,6-Tetrabenzoyloxy-7-octene (**13**): $[\alpha]_D^{25}$ −16.90° (*c*=1.0, $CHCl_3$). IR ($CHCl_3$): 1725, 1600, 1450, 1270, 1110, 1070, 1025 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.20 (1H, ddd, *J*=14.4, 6.1, 4.9 Hz), 2.31 (1H, dt, *J*=14.6, 5.6 Hz), 2.41 (1H, ddd, *J*=14.6, 7.6, 2.9 Hz), 2.43 (1H, ddd, *J*=14.4, 7.1, 2.7 Hz), 4.48 (1H, dd, *J*=12.0, 5.9 Hz), 4.59 (1H, dd, *J*=12.0, 3.7 Hz), 5.12 (1H, d, *J*=10.5 Hz), 5.27 (1H, d, *J*=17.3 Hz), 5.51 (1H, quintet, *J*=6.8 Hz), 5.68 (2H, m), 5.86 (1H, ddd, *J*=17.3, 10.5, 6.4 Hz), 7.33—7.56 (12H), 7.94—8.04 (8H). FABMS *m/z*: 593 (MH^+). HRFABMS *m/z*: Calcd for $C_{36}H_{32}O_8$: 593.2173. Found: 593.2148.

(2*S*,4*R*,6*R*)-1,2,4,6-Tetrabenzoyloxy-7-octene (**14**): $[\alpha]_D^{25}$ −22.68° (*c*=0.98, $CHCl_3$). IR ($CHCl_3$): 1720, 1600, 1450, 1270, 1120, 1070, 1025 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.31 (3H, m), 2.40 (1H, ddd, *J*=14.8, 9.1, 4.0 Hz), 4.48 (1H, dd, *J*=11.8, 5.7 Hz), 4.61 (1H, dd, *J*=11.8, 3.7 Hz), 5.21 (1H, d, *J*=10.4 Hz), 5.34 (1H, d, *J*=17.1 Hz), 5.50 (1H, m), 5.64 (2H, m), 5.93 (1H, ddd, *J*=17.1, 10.4, 5.1 Hz), 7.22—7.56 (12H), 7.85—8.02 (8H). FABMS *m/z*: 593 (MH^+).

(2*S*,4*R*,6*S*)-1,2,4,6-Tetrabenzoyloxy-7-octene (**15**): $[\alpha]_D^{25}$ −35.40° (*c*=1.0, $CHCl_3$). IR ($CHCl_3$): 1720, 1600, 1450, 1265, 1200, 1110, 1070, 1025 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.15 (1H, dt, *J*=14.5, 5.7 Hz), 2.24 (1H, ddd, *J*=14.8, 8.7, 3.4 Hz), 2.45 (1H, ddd, *J*=14.8, 9.4, 3.7 Hz), 2.48 (1H, dt, *J*=14.5, 7.4 Hz), 4.47 (1H, dd, *J*=11.8, 5.7 Hz), 4.59 (1H, dd, *J*=11.8, 3.7 Hz), 5.19 (1H, d, *J*=10.4 Hz), 5.32 (1H, d, *J*=17.1 Hz), 5.50 (1H, m), 5.62 (1H, m), 5.69 (1H, m), 5.91 (1H, ddd, *J*=17.1, 10.4, 6.1 Hz), 7.25—7.55 (12H), 7.80—8.00 (8H). FABMS *m/z*: 593 (MH^+).

(2*S*,4*S*,6*S*)-1,2,4,6-Tetrabenzoyloxy-7-octene (**16**): $[\alpha]_D^{25}$ −25.40° (*c*=1.01, $CHCl_3$). IR ($CHCl_3$): 1720, 1600, 1450, 1270, 1220, 1125, 1070, 1025 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.21—2.36 (3H, m), 2.45 (1H, dt, *J*=14.5, 7.3 Hz), 4.51 (1H, dd, *J*=12.4, 6.1 Hz), 4.62 (1H, dd, *J*=12.4, 3.5 Hz), 5.17 (1H, d, *J*=16.9 Hz), 5.32 (1H, d, *J*=10.4 Hz), 5.53 (1H, m), 5.63 (2H, m), 5.91 (1H, ddd, *J*=16.9, 10.4, 6.1 Hz), 7.20—7.60 (12H), 7.80—8.05 (8H). FABMS *m/z*: 593 (MH^+).

References and Notes

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