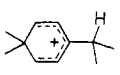
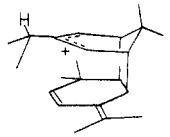
amounts of an insoluble white material which we assume is polymer were formed at lower concentrations and were removed by filtration through alumina before analysis of the products. **4** is obviously an acid-catalyzed rearrangement product of **1** and is formed efficiently when **1** is treated with acids such as TFA at room temperature. In neat CH_2Cl_2, dropwise addition of $3^+SbCl_6^-$ to 0.067 M **1** at −78 °C required 5.6 mol % oxidant before starting material was consumed, as indicated visually by the persistance of the green color of 3^+, and only cumene **4** was isolated after removal of polymer. Addition of 1% each of TFAA and TFA to the solvent (100:1:1) caused **2** and **5** to appear along with **4** in roughly similar amounts, ^1H NMR integration giving 30%, 40%, and 30%, respectively. Careful control of the conditions led to substantial improvement in the yield of **2**. Treatment of 0.5 M **1** in 100:10:1 CH_2Cl_2/TFAA/TFA at −86 °C required 12 mol % 3^+ to consume **1**, and workup gave a 12% loss of material, presumably as polymer. The product ratios by ^1H NMR were 77% **2**, 18% **4**, and 5% **5**, corresponding to a 68% crude yield of **2**. Pure **2** was obtained by preparative TLC in 57% yield. If **1** is subjected to the reaction conditions without 3^+, it is recovered unchanged. Thus it appeared that dimerization of **1** to **2** was catalyzed by one-electron oxidation conditions. Acid catalysis for the formation of **2** was, however, established by the proper control experiment. Treatment of 0.3 M **1** in 100:10:1 CH_2Cl_2/TFAA/TFA at −86 °C with HBF_4–Et_2O gave an 80% yield of **2** after preparative TLC; 12% **4** was observed but no **5** was detected. Control experiments established the need for TFA and TFAA in the reaction mixture to obtain **2**; only **4** was observed in their absence. We believe it noteworthy that **5** appears only under cation radical conditions. Its formation from 1^+ entails bonding between the terminal CMe_2 groups (a "radical" reaction), two methyl group shifts, and two deprotonations ("carbonium ion" reactions), producing acid which catalyzes the production of **2** and **4**, if enough acid for this purpose is not inadvertently introduced along with the 3^+.[4] We have no information on the timing of the bond formations and cleavages.

Protonation of **1** presumably gives pentadienyl cation **6**, which rearranges to produce **4** in the absence of trifluoroacetate groups but goes on to give **2** in their presence, for reasons that are as yet unknown. **6** could react with **1** by a concerted [4 + 2] cycloaddition[5,6] to give the diene–allyl cation intermediate **7**. Such additions are



6



7

well-established for 2,5-cyclohexadienone derivatives, but we are unaware of any examples for hydrocarbons. Closure of **7** to **2** might involve stepwise [2 + 2] cycloaddition of its alkene and allyl cation fragments, which has limited precedent,[6,7] followed by deprotonation of the resulting tertiary cation. A particularly interesting feature of the production of **2** is that whether the cage structure can be produced has already been determined by the first cycloaddition, where formation of the endo intermediate **7** is apparently substantially favored over the exo form. The steric interactions of the gem-4,4-dimethyls with the six-membered rings in the transition-state complex of **1** and **6** would inhibit formation of the exo isomer. There is very little precedent for the conversion of **1** to its crisscross dimer **2**. The closest structural analogy we have found is the dimerization of norbornadienes[8] to analogous crisscross dimers in transition-metal-catalyzed (Fe, Rh) reactions which go in low yield.[9]

Registry No. **1**, 63577-41-3; **2**, 104423-54-3; $3^+SbCl_6^-$, 58047-17-9; **4**, 4132-77-8; **5**, 104423-55-4.

(4) (a) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085. (b) Gassman, P. G.; Singleton, D. A. *Ibid.* **1984**, *106*, 7993.
(5) Walls, F.; Padilla, J.; Joseph-Nathan, P.; Giral, F.; Escobar, M.; Romo, J. *Tetrahedron* **1966**, *22*, 2387.
(6) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
(7) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1.
(8) (a) Lemal, D. M.; Shim, K. S. *Tetrahedron Lett.* **1961**, 368. (b) Bird, C. W.; Colinese, D. L.; Cookson, R. C.; Hudec, J.; Williams, R. O. *Ibid.* **1961**, 373. (c) Acton, N.; Roth, R. J.; Katz, T. J.; Frank, J. K.; Maier, C. A.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 5446. (d) Marchand, A. P.; Earlywine, A. D. *J. Org. Chem.* **1984**, *49*, 1660.
(9) **Acknowledgement**: We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Amoco Oil Company for partial financial support of this research. We thank Dr. Bruce Adams for help with high field NMR experiments and the referees for encouraging us to reconsider acid catalysis for the production of **2**.

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Electrochemical Glycosylation Method

Summary: Hydroxyl-protected and -unprotected glycosyl aryloxides react with alcohols under mild electrolytic conditions to give the corresponding glycosides.

Sir: Glycosylation of alcohols has conventionally been achieved by heterolysis of glycosyl derivatives having an anomeric leaving group (Gly-X) with Brønsted or Lewis acid promoters (eq 1).[1] Besides such two-electron ex-

$$\text{Gly-X} \xrightarrow{-X^-} \text{Gly}^+ \xrightarrow{\text{ROH}} \text{Gly-OR} \quad (1)$$

$$\text{Gly-X} \xrightarrow{-e} \text{Gly-X}^{\bullet+} \xrightarrow{-X^\bullet} \text{Gly}^+ \xrightarrow{\text{ROH}} \text{Gly-OR} \quad (2)$$

change processes, cleavage of Gly–X bond stimulated by a one-electron-transfer process is an attractive alternative for this purpose. Equation 2 outlines the possible $S_{ON}1$ pathway[2] involving one-electron-oxidized substrates. Described herein is the first electrochemical method based on such strategy.[3,4]

When electricity was passed through a mixture of an *aryl* glycoside (**1**), alcoholic nucleophile (1:1 to 1:2 molar ratio), and electrolyte in an appropriate polar solvent placed in an undivided cell under a constant voltage by

(1) Pertinent reviews: Wulff, G.; Röhle, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 157. Igarashi, K. *Adv. Carbohydr. Chem. Biochem.* **1977**, *34*, 243. Bochkov, A. F.; Zaikov, G. E. *Chemistry of the O-Glycosidic Bond: Formation and Cleavage*; Pergamon: Oxford, 1979. Tsutsumi, H.; Ishido, Y. *J. Synth. Org. Chem. Jpn.* **1980**, *38*, 473. Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155. Koto, S.; Morishima, N.; Zen, S. *J. Synth. Org. Chem. Jpn.* **1983**, *41*, 701.
(2) For nomenclature, see: Alder, R. W. *J. Chem. Soc., Chem. Commun.* **1980**, 1184.
(3) For related photochemical processes, see: (a) Hashimoto, S.; Kurimoto, I.; Fujii, Y; Noyori, R. *J. Am. Chem. Soc.* **1985**, *107*, 1427. (b) Timpa, J. D.; Griffin, G. W. *Carbohydr. Res.* **1984**, *131*, 185.
(4) An electrochemical ester exchange reaction of acetoxy sugars by a different mechanism has been recorded: Imagawa, T.; Nakashita, Y.; Kawanishi, M. *Chem. Lett.* **1980**, 1609.

0022-3263/86/1951-4320$01.50/0

Table I. Electrochemical Glycosylation[a]

entry	substrate 1 R	substrate 1 Ar	substrate 1 α or β	nucleophile (equiv)	conditions V[b]	conditions time, h	product 2 % yield[c]	product 2 α/β
1	CH_3CO	C_6H_5	β	CH_3OH (1.4)	2.0	3	79	<3:97[d]
2	CH_3	C_6H_5	α	CH_3OH (1.2)	2.0	2	84	22:78[d]
3	$C_6H_5CH_2$	C_6H_5	β	CH_3OH (1.7)	2.0	4	81	37:63[e]
4[f]	$C_6H_5CH_2$	C_6H_5	β	CH_3OH (1.6)	2.0	8	92	35:65[e]
5	$C_6H_5CH_2$	2,4,6-$(CH_3)_3C_6H_2$	β	CH_3OH (1.0)	1.5	1	90	34:69[e]
6	$C_6H_5CH_2$	2,4,6-$(CH_3)_3C_6H_2$	β	**3** (R = $C_6H_5CH_2$) (2.0)	1.5	2	68	29:71[e]
7	$C_6H_5CH_2$	2,4,6-$(CH_3)_3C_6H_2$	β	c-$C_6H_{11}OH$ (1.1)	1.5	3	70	46:54[e]
8	$C_6H_5CH_2$	2,4,6-$(CH_3)_3C_6H_2$	β	t-C_4H_9OH (1.6)	1.5	5	58	34:66[e]
9	H	C_6H_5	α	CH_3OH (1.3)	2.0	1.5	93	79:21[g]
10	H	C_6H_5	β	CH_3OH (1.0)	2.0	2	77	75:25[g]
11	H	C_6H_5	α	**3** (R = CH_3) (1.6)	2.3	2	66	50:50[d]
12	H	2,4,6-$(CH_3)_3C_6H_2$	β	C_2H_5OH (1.3)	1.5	1.5	78	63:37[h]
13	H	2,4,6-$(CH_3)_3C_6H_2$	β	$(CH_3)_3CCH_2OH$ (1.4)	1.5	1	75	61:39[h]
14	H	2,4,6-$(CH_3)_3C_6H_2$	β	$(CH_3)_2CHOH$ (1.2)	1.5	2	76	61:39[h]
15	H	2,4,6-$(CH_3)_3C_6H_2$	β	c-$C_6H_{11}OH$ (1.1)	1.5	1	85	59:41[h]
16	H	2,4,6-$(CH_3)_3C_6H_2$	β	t-C_4H_9OH (1.1)	1.5	2.5	59	52:48[h]

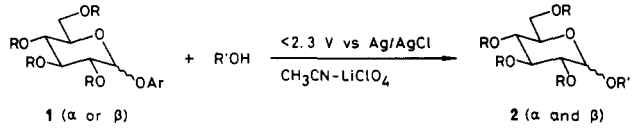
[a] Unless otherwise stated, the reaction was conducted in acetonitrile at room temperature. [b] Voltage vs. Ag/AgCl reference electrode. [c] Isolated yield. [d] Determined by ^1H NMR. [e] Determined by HPLC. [f] Reaction was conducted in butyronitrile. [g] Determined by ^1H NMR after peracetylation. [h] Determined by GLC analysis after pertrimethylsilylation.

Table II. Oxidation Potentials of Aryl Glycosides[a]

aryl glycoside 1 Ar	aryl glycoside 1 R	$E_{ox}^{p/2}$, V, vs. Ag/AgCl
C_6H_5	CH_3CO	1.96
C_6H_5	$C_6H_5CH_2$	1.96
C_6H_5	H	1.89
C_6H_5	CH_3	1.63
2,4,6-$(CH_3)_3C_6H_2$	$C_6H_5CH_2$	1.26
2,4,6-$(CH_3)_3C_6H_2$	H	1.07

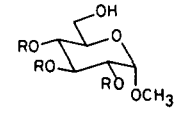
[a] Determined by cyclic voltammetry on the glassy carbon electrode, sodium perchlorate (0.01 M) in acetonitrile solution.

using Pt foils as electrodes, the corresponding glycosides (**2**) were obtained. Table I lists examples. Efficiency of



1 (α or β) **2** (α and β)

the electrochemical reaction is influenced by many reaction parameters. Acetonitrile or butyronitrile was the best solvent so far examined. Lithium perchlorate is recommended as electrolyte.[5] The nature of the leaving groups, particularly the redox properties (Table II), is extremely important. For example, glucosyl phenoxide (**1**, Ar = C_6H_5, R = CH_3) or the trimethylphenoxide (**1**, Ar = 2,4,6-$(CH_3)_3C_6H_2$, R = $C_6H_5CH_2$) underwent smoothly the exchange reaction with methanol, whereas the corresponding glucosyl acetate or methoxide showing no oxidation tendency below 2.0 eV (cyclic voltammetry) was totally inert under the standard reaction conditions. Thus if glycosylation were to proceed, it would be at voltages higher than the oxidation potentials of the substrates. As nucleophiles, various alcohols, even *tert*-butyl alcohol or neopentyl alcohol, were employable. Disaccharides are also obtainable by this method (entries 6 and 11). However, use of C-nucleophiles such as cyanotrimethylsilane or allyltrimethylsilane gave little (ca. 20%) or no glycosylation products. Interesting is the behavior of the hydroxyl-unprotected substrates of type **4**. Such compounds do not undergo dimerization, polymerization, or intramolecular cyclization leading to 1,6-anhydroglucose. Combination of unprotected substrate **4** (Ar = C_6H_5) and fully protected derivative **3** (R = CH_3), however, gave the corresponding disaccharide in a reasonable yield (entry 11).[6]



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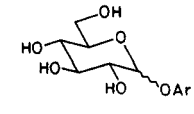

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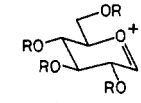

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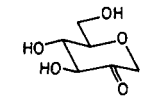

6

Apparently the present glycosylation proceeds via oxocarbenium ion intermediate **5**, generated from the radical cation of the easily oxidizable aryloxy substrate **1**.[7] The reaction of peracetylated D-glucosyl phenoxide (**1**, Ar = C_6H_5, R = CH_3CO) and alcohols gave only β-glucosyl products by the 1,2-trans effect (entry 1). The substrates bearing "nonparticipating" protective groups afforded mixtures of the α- and β-anomers with moderate β-stereoselection (entries 2–8). On the other hand, hydroxyl-unprotected glucosides of type **4** gave the α-glycosylation products predominantly (entries 9–16).[6] The observed stereoselectivity is a result of kinetic control, because (1) the α/β ratio is not affected appreciably by the stereochemistry of the starting materials and (2) the substrates and products, **1** and **2**, are stereochemically stable and do not undergo α ⇌ β stereomutation under the electrolytic conditions. In the absence of any alcoholic nucleophiles or in the presence of only poor nucleophiles, deprotonation occurs from **5** (R = H), for example, to give **6**.[8]

Thus this electrochemical glycosylation provides a rare example of $S_{ON}1$ reaction.[2] The present method is economical and operationally simple and, complementarily to the existing procedures, offers a useful tool in carbohydrate synthesis.

Typical Procedure for the Electrochemical Glycosylation. Methyl 2,3,4,6-tetra-*O*-benzyl-D-glucoside. A

(5) Sodium perchlorate may be used. But debenzylation of the substrate **1** (Ar = C_6H_5, R = $C_6H_5CH_2$) occured to some extent. See: Mayeda, E. A.; Miller, L. L.; Wolf, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 6812.

(6) Such unique selectivity has some precedent: Hanessian, S.; Bacquet, C.; Lehong, N. *Carbohydr. Res.* **1980**, *80*, C17.

(7) Fates of the aryloxy radicals are complicated. Phenols, quinones, and the dimeric coupling products among others were characterized.

(8) In addition, some glucose was formed because of the presence of a trace amount of water in acetonitrile solvent.

solution of 1β (71.1 mg, 0.115 mmol), methanol (6.5 mg, 0.203 mmol), and lithium perchlorate (234.7 mg) in anhydrous acetonitrile (10 mL) was placed in an undivided cell fitted with two Pt foils (1 cm × 2 cm) and an Ag/AgCl reference electrode. Electricity was then passed under a constant voltage, 2.0 V vs. Ag/AgCl, at 30 °C for 4 h. After confirmation of disappearance of 1 (TLC monitoring), the mixture was concentrated under vacuum. The residue was mixed with ether (30 mL) and then with water (20 mL). The organic layer was washed with brine (10 mL), dried over Na_2SO_4, and evaporated. Chromatography on a silica gel column (8:1 hexane–ethyl acetate) gave **2** (R = $C_6H_5CH_2$, R′ = CH_3) (51.5 mg, 81% yield), α/β = 37:63.

Registry No. β-1 (R = CH_3CO, Ar = C_6H_5), 4468-72-8; α-1 (R = CH_3, Ar = C_6H_5), 3149-61-9; β-1 (R = $C_6H_5CH_2$, Ar = C_6H_5), 72366-52-0; β-1 (R = $C_6H_5CH_2$, Ar = 2,4,6-$(CH_3)_3C_6H_2$, 104550-44-9; α-1 (R = H, Ar = C_6H_5), 4630-62-0; β-1 (R = H, Ar = C_6H_5), 1464-44-4; β-1 (R = H, Ar = 2,4,6-$(CH_3)_3C_6H_2$, 31617-31-9; α-2 (R = CH_3CO, R′ = CH_3), 604-70-6; β-2 (R = CH_3CO, R′ = CH_3), 4860-85-9; α-2 (R = CH_3, R′ = CH_3), 605-81-2; β-2 (R = CH_3, R′ = CH_3), 3149-65-3; α-2 (R = $C_6H_5CH_2$, R′ = CH_3), 17791-37-6; β-2 (R = $C_6H_5CH_2$, R′ = CH_3), 19488-61-0; α-2 (R = $C_6H_5CH_2$, R′ = methyl 2,3,4-tri-*O*-benzyl-α-D-glucos-6-yl), 55094-26-3; β-2 (R = $C_6H_5CH_2$, R′ = methyl 2,3,4-tri-*O*-benzyl-α-D-glucos-6-yl), 56632-57-6; α-2 (R = $C_6H_5CH_2$, R′ = c-C_6H_{11}), 56632-55-4; β-2 (R = $C_6H_5CH_2$, R′ = c-C_1H_{11}), 56632-56-5; α-2 (R = $C_6H_5CH_2$, R′ = *t*-C_4H_9), 67525-69-3; β-2 (R = $C_6H_5CH_2$, R′ = *t*-C_4H_9), 78153-80-7; α-2 (R = H, R′ = CH_3), 97-30-3; β-2 (R = H, R′ = CH_3), 709-50-2; α-2 (R = H, R′ = methyl 2,3,4-tri-*O*-methyl-α-D-glucos-6-yl), 104550-45-0; β-2 (R = H, R′ = methyl 2,3,4-tri-*O*-methyl-α-D-glucos-6-yl), 104550-46-1; α-2 (R = H, R′ = C_2H_5), 19467-01-7; β-2 (R = H, R′ = C_2H_5), 3198-49-0; α-2 (R = H, R′ = $(CH_3)_3CCH_2$), 25320-97-2; β-2 (R = H, R′ = (CH_3),3CCH_2), 5285-03-0; α-2 (R = H, R′ = $(CH_3)_2CH$), 25320-92-7; β-2 (R = H, R′ = $(CH_3)_2CH$), 5391-17-3; α-2 (R = H, R′ = c-C_6H_{11}), 25320-98-3; β-2 (R = H, R′ = c-C_6H_{11}), 5284-99-1; α-2 (R = H, R′ = *t*-C_4H_9), 33538-53-3; β-2 (R = H, R′ = *t*-C_4H_9), 29074-04-2; **3** (R = $C_6H_5CH_2$), 53008-65-4; **3** (R = CH_3), 4153-24-6; **7**, 18311-26-7; CH_3OH, 67-56-1; c-$C_6H_{11}OH$, 108-93-0; *t*-C_4H_9OH, 75-65-0; C_2H_5OH, 64-17-5; $(CH_3)_3CCH_2OH$, 75-84-3; $(CH_3)_2CHOH$, 67-63-0; 2,4,6-trimethylphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucoside, 104550-47-2; penta-*O*-acetyl-β-D-glucose, 604-69-3; methyl 2,3,4-tri-*O*-benzyl-6-*O*-trityl-α-D-glucoside, 18685-93-3; methyl 2,3,4-tri-*O*-benzyl-6-*O*-acetyl-α-D-glucoside, 82231-38-7; methyl 2,3,4-tri-*O*-methyl-6-*O*-trityl-α-D-glucoside, 6984-43-6; phenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucoside, 72366-52-0.

Supplementary Material Available: Experimental details of compounds and methods used in this study (8 pages). Ordering information is given on any current masthead page.

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Total Synthesis of a Slightly Unnatural Product. Confirmation of the Stereostructure of the Archaebacterial C_{40} Diol by Synthesis of a Stereoisomer[1]

Summary: Diol **2** has been prepared by stereorational total synthesis; comparison of **2** with samples of naturally derived and synthetic diol 1 by 125-MHz ^{13}C NMR spectroscopy demonstrates that such stereoisomers can be distinguished by this technique and adds confirmation to the assigned stereostructure of the archaebacterial lipids derived from 1.

Sir: In a recent publication[2] we reported the stereorational total synthesis of diol 1 and advanced ^{13}C NMR evidence that it is identical with the so-called "archaebacterial C_{40} diol". In order to be fully confident that stereoisomers of the gross structure 1 can be distinguished by the analytical method used, and therefore of the identity of our synthetic material with the naturally derived diol, we thought it worthwhile to synthesize a stereoisomer of 1. Isomer **2** was chosen as the secondary synthetic target for two reasons. First, we reasoned that, of the many stereoisomers of 1, the ^{13}C NMR spectrum of **2** would be most like that of 1. Like 1, diol **2** has C_2 symmetry and can show a maximum of 20 ^{13}C NMR resonances. In addition, the stereochemical differences in these two isomers occur only at C-15 and C-18, far away from the functional ends of the chain. Second, structures 1 and **2** are the most likely stereoisomeric forms of the archaebacterial C_{40} diol on biosynthetic grounds.[2] In this paper, we report the synthesis of **2**, which is different by ^{13}C NMR spectroscopy from the naturally derived diol.

The synthetic strategy employed for the preparation of **2** was similar to that used for our earlier synthesis of 1—sequential aldol addition and Claisen rearrangement.[3] Evans' asymmetric aldol strategy[4] was used to acquire the desired chirality. As shown in Scheme I, the di-*n*-butylboron enolate of *N*-propionyloxazolidone **3** was condensed with acrolein to obtain an aldol, which was converted by four straightforward steps into allylic propionate **4**. This material was converted into unsaturated acids **5** and **6** by Ireland's modification of the Claisen rearrangement.[5] Isomer **5** (88% diastereomeric purity) resulted from rearrangement of the enolate produced from **4** by reaction with lithium diisopropylamide (LDA) in tetrahydrofuran (THF). Isomer **6** (86% diastereomeric purity) was obtained from rearrangement of the enolate produced from **4** by reaction with LDA in a mixture of THF and hexamethylphosphoric triamide (HMPA). Isomers **5** and **6** were converted into the C_{10} synthons **7** and **8**, respectively. Alkylation of the anion of **8** with iodide **7** produced the C_{20} compound **9**, which was converted by a four-step sequence into bromo ether **10**. The Grignard reagent derived from bromide **10** was oxidized with silver nitrate to give a bis(*tert*-butyldiphenylsilyl) ether of **2**. Deprotection of this substance provided **2**, contaminated by minor diastereomers.[6]

Compound **2** was compared by ^{13}C NMR spectroscopy[7] with an authentic sample of the C_{40} diol that was obtained

(1) This is part 37 in a series of publications on acyclic stereoselection; for part 36 see: Heathcock, C. H.; Davidsen, S. K.; Hug, K. T.; Flippin, L. A. *J. Org. Chem.* **1986**, *51*, 3027.

(2) Heathcock, C. H.; Finkelstein, B. L.; Aoki, T.; Poulter, C. D. *Science (Washington, DC)* **1985**, 229, 862.

(3) For other applications of the aldol-Claisen strategy for 1,5-stereoselection, see: (a) Heathcock, C. H.; Jarvi, E. T. *Tetrahedron Lett.* **1982**, *23*, 2825. (b) Heathcock, C. H.; Jarvi, E. T.; Rosen, T. *Tetrahedron Lett.* **1984**, *25*, 243. For an application of the strategy for 1,4-stereoselection, see: (c) Heathcock, C. H.; Finkelstein, B. L. *J. Chem. Soc., Chem. Commun.* **1983**, 919.

(4) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127.

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(6) Compounds **5** and **6** were used as obtained from the Claisen rearrangements (88% and 86% diastereomeric purity, respectively). Assuming no kinetic resolution in the coupling reactions leading to **9** and to the bis(*tert*-butyldiphenylsilyl) ether of **2**, it may be calculated that the final diol contains 57% of diastereomer **2** and smaller amounts of several other diastereomers. Only two of the minor isomers are calculated to be present to the extent of greater than 2%. Neither of these isomers (9.3% and 7.8%) are C_2-symmetric and both will theoretically give rise to 40 signals.

(7) We thank Mr. Eric Lodge, University of California, for assistance in obtaining the ^{13}C NMR spectrum.

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