Titanium Tetrachloride Mediated Addition of 1,8-Bis(trimethylsilyl)-2,6-octadiene to Aldehydes. A One-Step Control of Four Stereogenic Carbon Centers

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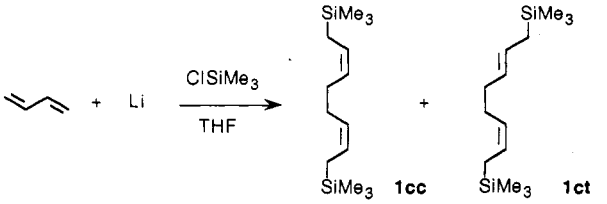
Received August 5, 1993 (Revised Manuscript Received January 4, 1994®)

The addition reaction of 1,8-bis(trimethylsilyl)-2,6-octadiene with aliphatic aldehydes in the presence of titanium tetrachloride affords 2,5-divinylhexane-1,6-diols with very high diastereoselectivity (up to 90%) and good yields (ca. 70–75%). In the case of benzaldehyde, the structure of the adduct was established as the *meso* isomer (1*S**,2*R**,5*S**,6*R**)-1,6-diphenyl-2,5-divinyl-1,6-hexanediol by single-crystal X-ray analysis.

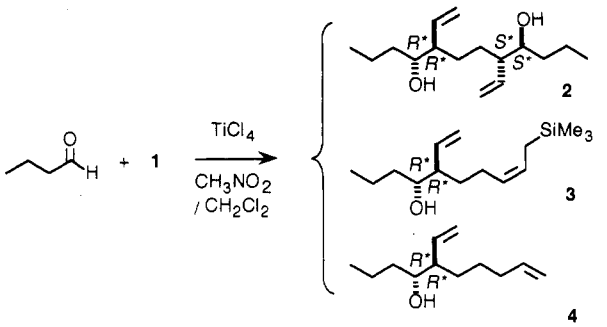
Stereoselectivity in C–C bond-forming reactions has frequently resulted in important progress in organic synthesis.[1] Lewis acid mediated reactions constitute an indispensable part of modern synthetic chemistry, especially in the art of acyclic stereocontrol.[2] Among a number of reactive intermediates, allylsilanes may claim to be important for achieving C–C bond formation by addition to aldehydes.[3] We report here on the Lewis acid catalyzed addition of 1,8-bis(trimethylsilyl)-2,6-octadiene (1) with aldehydes.

1,8-Bis(trimethylsilyl)-2,6-octadiene (BISTRO, 1) is readily obtained from 1,3-butadiene by reduction with lithium in the presence of chlorotrimethylsilane.[4] The material formed is actually a mixture of the (*Z*,*Z*) isomer (ca. 50%) **1cc**, the (*Z*,*E*) isomer (ca. 40%) **1ct**, and the (*E*,*E*) isomer (4%), contaminated with about 6% of 1,6-bis(trimethylsilyl)-2,7-octadiene (2:1 mixture of (2*Z*) and (2*E*) isomers). This byproduct can be removed by careful distillation with a spinning band column. In contrast to lithium, reduction of 1,3-butadiene with sodium leads to a much larger proportion of **1cc** (up to 80%).

In our previous work, we observed that $TiCl_4$-mediated addition of 1 (2.2 equiv; mixture resulting from Li reduction) to butanal gives rise to diol **2** (77% yield) with very high diastereoselectivity (up to 92%) and alcohols **3** (3% yield; two isomers, 9:1) and **4** (18% yield; diastereoselectivity up to 98%). The *Z* configuration of **3** is



determined by ^{13}C NMR (signal at 18.3 ppm for the carbon atom bearing the trimethylsilyl group) and ^{29}Si NMR (*Z*-γ-substitued allyltrimethylsilane, δ/TMS = ca. 1.25 ppm, (*E*) isomer, δ = ca. 0.5 ppm).



Similar results are observed with propanal (**5a**) (**6a**, 72% yield), isobutyraldehyde (**5b**) (**6b**, 71% yield), valeraldehyde (**5c**) (**6c**, 72% yield), isovaleraldehyde (**5d**) (**6d**, 77% yield), and *p*-nitrobenzaldehyde (**5f**). In the reaction of **5f**, three compounds were formed, diol **6f** (43% yield), and alcohols **7** (11% yield) and **8** (32% yield). In each addition, the silyl derivative **9** resulting from protodesilylation of **1** is also produced (ca. 7% yield).[4a] The presence of nitromethane (4 molar equiv) reduced or prevented the formation of alcohol **10**, which results from participation of the second allylsilane moiety during the initial reaction.[6]

The relative reactivity of **1cc** and **1ct** was determined by using an excess of 1 (2 equiv); the recovered BISTRO proved to be the (*Z*,*Z*) isomer **1cc** only. Thus, the minor (*Z*,*E*) isomer **1ct** is the more reactive one.

With the aim of determining the stereochemistry of the diols **2** or **6**, we attempted single-crystal X-ray analysis of **2**.[7] Unfortunately, neither compound led to a suitable crystalline product. Addition of **1** to benzaldehyde **5e** gave

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• Abstract published in *Advance ACS Abstracts*, March 1, 1994.

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(4) (a) Tubul, A.; Santelli, M. *Tetrahedron* **1988**, *44*, 3975. (b) Tubul, A.; Ouvrard, Ph.; Santelli, M. *Synthesis* **1991**, 173–176. (c) Ouvrard, Ph.; Tubul, A.; Santelli, M. *Tetrahedron Lett.* **1992**, *33*, 7519–7520. (d) Pellissier, H.; Tubul, A.; Santelli, M. *Tetrahedron Lett.* **1993**, *34*, 827–830. (e) Pellissier, H.; Michellys, P. Y.; Santelli. M. *Tetrahedron Lett.* **1993**, *34*, 1931–1934.

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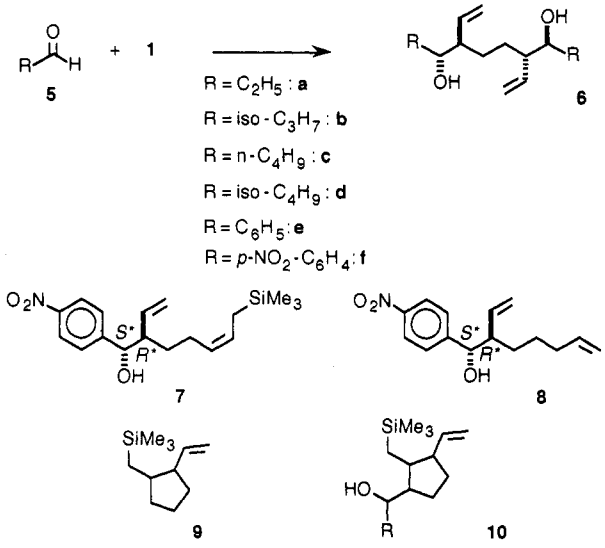
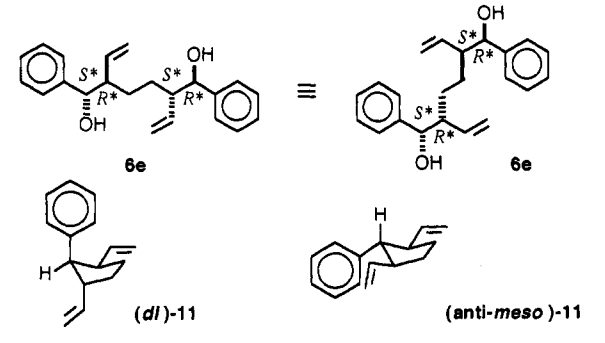
Table 1. Reaction of BISTRO (1) with Aldehydes

aldehyde	diol	yield, %	dr[a]
butanal	2	77	11.5:1
5a	6a	72	11.5:1
5b	6b	71	9:1
5c	6c	72	9:1
5d	6d	77	13:1
5e	6e	9	13:1
5f	6f	43	11.5:1

[a] Diastereomeric ratio, which was determined by ^{1}H NMR.



as major products the cyclopentanes *anti-meso*-**11** and *dl*-**11** (84% yield, inseparable mixture, 53:47) coming from a dialkylation process. Nevertheless, the diol **6e** was also formed (9%) and found to exist in a crystalline form. Structure determination by single-crystal X-ray diffraction gave the results shown by the perspective drawing of the molecule in Figure 1. The structural results show clearly that the stereogenic centers are C1(*S**), C2 (*R**), C5(*S**), and C6(*R**).[8]



In order to confirm the structure of diols **6a–d**, we tried to convert them in cyclic derivatives which can reveal the relative stereochemistry by ^{1}H NMR coupling constants. In particular, treatment of the diol **6b** by BuLi followed by phosgene addition gives rise to the corresponding cyclic carbonate **12b**. In the ^{1}H NMR spectrum of **12b**, protons at C-3 and C-8 appeared as a single signal, a doublet of

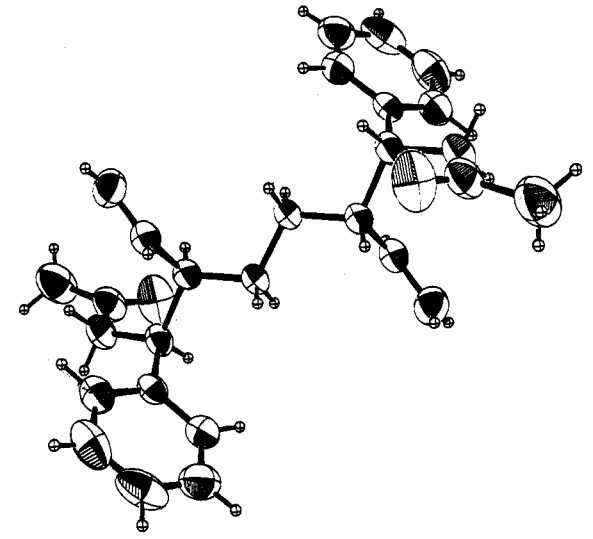
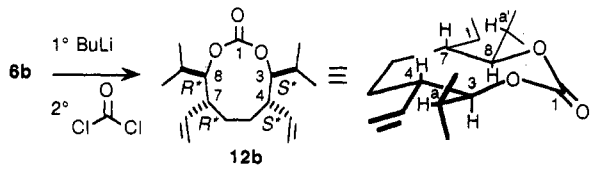


Figure 1. ORTEP plot of **6e**.

doublets ($J_{3,4} = J_{7,8} = 8.6$ Hz; $J_{3,a} = J_{3,a'} = 3.9$ Hz) at 4.71 ppm, in agreement with the proposed *meso* structure. Likewise protons at C-4 and C-7 were observed as a single signal at 2.31 ppm, and only nine signals were present in the ^{13}C NMR spectrum. Moreover, the $J_{3,4}$ coupling constant value was consistent with a pseudodiaxal arrangement in the idealized chair–chair conformation of C_s symmetry.[9]



Lewis acid catalyzed addition of crotylsilane to aldehydes is known to give high syn:anti ratios.[10,11] The structure of **6e** corresponds to a syn diastereoselectivity,

(7) **1** (*E,E* isomer) has been prepared by the reaction of hexamethyldisilane with butadiene in the presence of $PdCl_2(PhCN)_2$. Condensation of **1** with ethanal gave rise to the corresponding diol, but the stereochemistry was not described, see: Sakurai, H.; Eriyama, Y.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1984**, *264*, 229–237.

(8) Chiral centers of which the relative but not the absolute configuration is known are differentiated by prefixes *R**,*S**; see: *J. Org. Chem.* **1970**, *35*, 2849–2867.

(9) According to Hendrickson there are three idealized conformations of C_s symmetry for cyclononane: the boat-chair, the chair-boat, and the chair-chair; Hendrickson, J. B. *J. Am. Chem. Soc.* **1964**, *86*, 4854–4866. See also: (a) Anet, F. A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7172–7178. (b) Dorofeeva, O. V.; Mastryukov, V. S.; Allinger, N. L.; Almenningen, A. *J. Phys. Chem.* **1990**, *94*, 8044–8048. (c) Evans, D. G.; Boeyens, J. C. A. *Acta Cryst.* **1990**, *B46*, 524–532.

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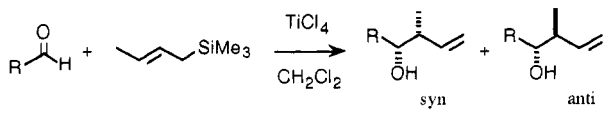
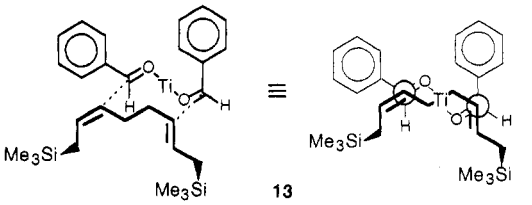
that is, each allylsilane moiety of 1 reacts with the same selectivity as that shown by γ-substituted allylsilanes.

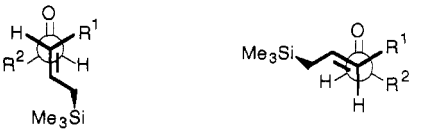


Lewis acid promoted additions of allylsilanes to aldehydes proceed via a nonchelated acyclic transition state. According to Yamamoto[12] and Hayashi–Kumada,[11a-c] the antiperiplanar arrangement, in which the aldehyde substituent and the γ-substituent of the allylsilane are anti, represents the lowest energy transition state. Moreover, for Lewis acid catalyzed additions of certain allylsilanes to aldehydes, a synclinal arrangement of the reacting olefin has been postulated.[13]

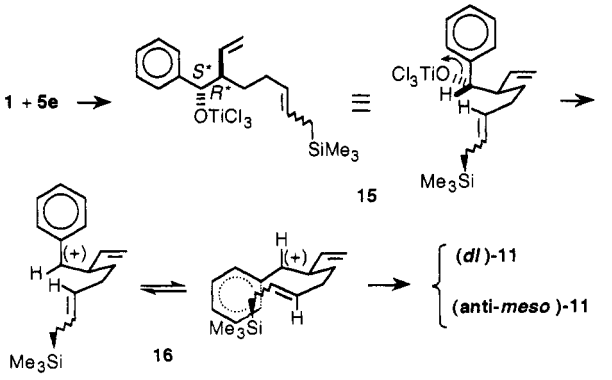
The high diastereoselectivity observed in the reaction of BISTRO, requires that the addition of the (*Z*,*E*) isomer **1ct** occurs on the complex $(RCHO)_2$–$TiCl_4$. Such complexes are well known[14] and have been previously invoked in the course of Lewis acid mediated reactions.[15] Examining possible transition states, we anticipated that if the titanium moiety could act as effective "template" resulting in a polydentate rigid transition state, the extremely efficient stereoselectivity could be explained.

We should note that the complex (benzaldehyde)$_2$–$TiCl_4$ shows remarkable levels of discrimination between the isomers of 1, as our experiments demonstrate that it effectively recognizes the delicate difference in steric factors of the two possible allylsilane partners.[16] The relative stereochemistry of **6e** can be readily explained assuming a staggered transition state for each addition as in **13** in which the complex (benzaldehyde)$_2$–$TiCl_4$ has a cis arrangement of the two ligands.[17,18] However, one ligand has the phenyl group anti to the titanium and in the other syn. In a recent study, Faller has observed a rapid interconversion between the syn and anti configurations in the complex $[HC(py)_3W(NO)_2(\eta^1$-benzaldehyde$)]$-$(SbF_6)_2$.[19,20] An ^1H NMR study was undertaken to investigate the complexation between benzaldehyde and $TiCl_4$. At −65 °C, when benzaldehyde (1 equiv) was added to a solution of $TiCl_4$ (0.5 equiv) in CD_2Cl_2, two signals were observed for the aldehyde proton at δ 10.07 and 9.98 (uncomplexed aldehyde) (relative intensity 4:1). The staggered transition states involved in **13** have an antiperiplanar structure (**14-*Z***) for the (*Z*)-allylsilane moiety and a synclinal structure (**14-*E***) for the (*E*)-allylsilane one. These transition structures must be favored for steric reasons in comparison with the possible other ones.





We may be certain that the formation of the cyclopentane hydrocarbon **11** results from Lewis acid induced ionization of the titanium alcoholate **15** to benzyl carbocation **16**, followed by ring closure. The absence of corresponding divinylcyclopentane from the reaction of 1 with aliphatic aldehydes or with *p*-nitrobenzaldehyde rules out a direct displacement on the Lewis acid complex **15**. From benzyl cation **16**, an unselective cyclization occurs by addition of the second allylsilane moiety.



Finally, the remarkable ease of preparation of 1 on a 2 M scale by a simple and inexpensive process, as well as the good yield and the unprecedented levels of diastereoselectivity of its addition reaction with aldehydes, enhances significantly the interest of our results.[21]

Experimental Section

General. All reactions were run under argon in oven-dried glassware. TLC was performed on silica gel 60 F_{254}. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 200 or 400 and

(12) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107–7109.

(13) A preferred synclinal arrangement has been suggested for an intramolecular addition leading to a bicyclo[2.2.2] homoallylic alcohol, see ref 11d,f,h,i (see also, ref 11g). The chelation-controlled addition of β-methyl substituted (*E*)-crotylsilanes to α-(benzyloxy)acetaldehyde afforded an anti homoallylic alcohol as major diastereomer. This stereochemical outcome has been rationalized with a synclinal TS; see refs 11j,o,q.

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(15) Keck, G. E.; Castellino, S. *J. Am. Chem. Soc.* **1986**, *108*, 3847–3849. (b) Denmark, S. E.; Almstead, N. G. *Tetrahedron* **1992**, *48*, 5565–5578. (c) Reetz, M. T.; Raguse, B.; Marth C. F.; Hügel, H. M.; Bach, T.; Fox, D. N. A. *Tetrahedron* **1992**, *48*, 5731–5742. (d) Cf. the dramatic changes in diastereoselectivity with the quantity of titanium tetrachoride used in Lewis acid mediated reactions of allylsilane with α-amino aldehydes, see: Kiyooka, S.; Nakano, M.; Shiota, F.; Fujiyama, R. *J. Org. Chem.* **1989**, *54*, 5409–5411.

(16) For examples of asymmetric aldol reactions of titanium enolates with the benzaldehyde–$TiCl_4$ complex, see: Yan, T.-H.; Tan, C.-W.; Lee, H.-C.; Lo, H.-C.; Huang, T.-Y. *J. Am. Chem. Soc.* **1993**, *115*, 2613–2621.

(17) The general structure of the postulated complex is similar to that of the diester–titanium tetrachloride chelate complexes, see refs 14c–f.

(18) These transition-state arrangements are traditionally depicted as Newman projections along the axis of the forming C–C bond.

(19) Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579–1586.

(20) For a well-documented discussion on the structure of Lewis acid–aldehyde complexes in solution, see: (a) Denmark, S. E.; Henke, B. R.; Weber, E. *J. Am. Chem. Soc.* **1987**, *109*, 2512–2514. (b) Denmark, S. E.; Almstead, N. G. *Tetrahedron* **1992**, *48*, 5565–5578. (c) Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1993**, *115*, 3133–3139.

(21) (a) To our knowledge, 1 is the only multicoupling reagent which display high stereoselectivity. (b) Symmetrical di-Grignard reagents and 1,*n*-heterobimetallic reagents do not react selectively, see: AchyuthaRao, S.; Knochel, P. *J. Org. Chem.* **1991**, *56*, 4591–4593.

50 or 100 MHz, respectively. Carbon–proton couplings were determined by DEPT sequence experiments.[22] Diastereoselectivity was determined by GC or ^{1}H NMR analyses prior to any purification.

Materials. Commercially available aldehydes were distilled before use. CH_2Cl_2 was distilled from P_2O_5.

1,8-Bis(trimethylsilyl)-2,6-octadiene (BISTRO) was prepared according to the previously described procedure.[4a] The spectral properties are as follows. IR (gas): 3015, 2962, 1255, 1159, 852 cm^{-1}, (*Z*) isomers 695 cm^{-1}, (*E*) isomers 964 cm^{-1} (see, ref 23). (*Z,Z*) isomer **1cc**: ^{1}H NMR δ 5.5–5.3 (4, m), 2.12 (4, br s), 1.49 (4, d, *J* = 7.9 Hz), 0.02 (18, s); ^{13}C NMR δ 127.3 (d), 125.7 (d), 27.5 (t), 18.6 (t), –1.6 (q). (*Z,E*) isomer **1ct**: ^{1}H NMR δ 5.5–5.3 (4, m), 2.12 (4, br s), 1.48 (2, d, *J* = 7.9 Hz), 1.41 (2, d, *J* = 7.5 Hz), 0.20 (9, s), 0.00 (9, s); ^{13}C NMR δ 128.7 (d), 127.3 (d), 126.3 (d), 125.5 (d), 33.2 (t), 27.7 (t), 22.7 (t), 18.6 (t), –1.6 (q), –1.8 (q). ^{29}Si NMR δ/TMS (INEPT sequence): **1cc**, 1.23, **1ct**, 1.27, 0.46.

Representative Procedure for the Addition of BISTRO (1) to Aldehydes. A three-necked flask equipped with a thermometer, septum cap, magnetic stirring bar, and argon outlet was charged with anhydrous CH_2Cl_2 (23 mL) and anhydrous nitromethane (3.2 mL, 60 mmol). The solution was cooled to –60 °C and $TiCl_4$ was added (1.7 mL, 15.5 mmol) and then aldehyde (15 mmol) in CH_2Cl_2 (2 mL). After 15 min of stirring at –70 °C, the solution was cooled at –90 °C and BISTRO (7.62 g, 30 mmol) in CH_2Cl_2 (3 mL) was added over 10 min. The resulting solution was stirred at –85 °C and at –60 °C for the indicated times. After this time, the reaction was complete as indicated by TLC analysis. The reaction was quenched by addition of an aqueous saturated NH_4Cl solution (40 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The extracts were washed until neutrality, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by chromatography on silica gel, eluting with a gradient of pentane–ether; diols were eluted with pentane–ether 4:1.

(4*R,5*R**,8*S**,9*S**)-5,8-Divinyl-4,9-dodecanediol (2)** was prepared by addition of **1** to butanal (1.08 g) (1 h at –90 °C and then 4 h at –60 °C). The crude product was chromatographed on silica gel (pentane, pentane–ether, 92:8 (**3**, **4**) to 80:20 (**2**)). **2** (obtained as major diastereomer, >92:8) (1.47 g, 77%): white crystals, mp 87 °C; IR (Nujol) 3500–3200, 1645, 915 cm^{-1}; ^{1}H NMR δ 5.68–5.47 (2, m), 5.18–5.00 (4, m), 3.45 (2, m), 2.04 (2, m), 1.6–1.07 (14, m), 0.90 (6, t, *J* = 6.1 Hz); ^{13}C NMR δ 139.4 (d), 139.3 (d), 116.9 (t), 116.8 (t), 74.0 (d), 73.8 (d), 51.1 (d), 50.6 (d), 36.2 (t), 36.1 (t), 27.9 (t), 27.3 (t), 19.1 (t) (2C), 14.0 (q) (2C). Anal. Calcd for $C_{16}H_{30}O_2$: C, 75.54; H, 11.89. Found: C, 75.50; H, 11.83.

(*Z*)-(6*R,7*R**)-1-(Trimethylsilyl)-6-vinyl-2-decen-7-ol (3)** (obtained as major diastereomer, 92:8) (115 mg, 3%): IR (neat) 3400, 3080, 3010, 1645, 1250, 1000, 915, 870–840 cm^{-1}; ^{1}H NMR δ 5.61 (1, ddd, *J* = 16.85, 10.40, 9.20 Hz), 5.47–5.04 (4, m), 3.53–3.46 (1, m), 2.17–1.87 (3, m), 1.65–1.21 (7, m), 0.92 (3, t, *J* = 6.50 Hz), 0.00 (9, s); ^{13}C NMR δ 139.3 (d), 127.2 (d), 125.4 (d), 116.8 (t), 73.8 (d), 50.5 (d), 36.2 (t), 30.0 (t), 24.7 (t), 19.1 (t), 18.3 (t), 14.0 (q), –1.9 (q) (3C); minor isomer, 138.6 (d), 127.1 (d), 125.5 (d), 117.5 (t), 73.3 (d), 49.8 (d), 36.9 (t), 30.9 (t), 24.7 (t), 18.9 (t), 18.3 (t), 14.0 (q), –1.93 (q) (3C); ^{29}Si NMR δ/TMS (INEPT sequence) 1.27. Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88. Found: C, 71.07; H, 12.03.

(4*R,5*R**)-5-Vinyl-9-decen-4-ol (4)** (obtained as major diastereomer, >98:2) (490 mg, 18%): IR (neat) 3400, 3080, 1645, 1000, 915 cm^{-1}; ^{1}H NMR δ 5.90–5.70 (1, m), 5.6 (1, ddd, *J* = 16.85, 10.45, 9.23 Hz), 5.15–4.90 (4, m), 3.53–3.45 (1, m), 2.15–1.99 (2, m), 1.65–1.20 (8, m), 0.92 (3, t, *J* = 6.5 Hz); ^{13}C NMR δ 139.3 (d), 138.8 (d), 116.9 (t), 114.4 (t), 74.0 (d), 50.8 (d), 36.1 (t), 33.8 (t), 29.4 (t), 26.7 (t), 19.2 (t), 14.0 (q). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.85; H, 12.28.

(3*R,4*R**,7*S**,8*S**)-4,7-Divinyl-3,8-decanediol (6a)** was prepared by addition of **1** to propanal (**5a**) (870 mg) (1 h at –90 °C and then 4 h at –60 °C). **6a** (obtained as major diastereomer, >92:8) (1.22 g, 72%): white crystals, mp 102–104 °C; IR (Nujol) 3450, 1640 cm^{-1}; ^{1}H NMR δ 5.67–5.45 (2, m), 5.19–5.03 (4, m), 3.40 (2, m), 2.07 (2, m), 1.66–1.20 (8, m), 0.96 (6, t, *J* = 7.3 Hz); ^{13}C NMR δ 139.4 (d), 139.35 (d), 116.55 (t), 116.46 (t), 75.6 (d), 75.3 (d), 50.8 (d), 50.3 (d), 27.3 (t), 26.8 (t) (2C) , 26.7 (t), 10.1 (q) (2C). Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 74.36; H, 11.48.

(3*R,4*R**,7*S**,8*S**)-2,9-Dimethyl-4,7-divinyl-3,8-decanediol (6b)** was prepared by addition of **1** to 2-methylpropanal (**5b**) (1.08 g) (1 h at –85 °C and 12 h at –60 °C). **6b** (obtained as major diastereomer, 9:1) (1.35 g, 71%): white crystals, mp 115–117 °C; IR (Nujol) 3640, 1640 cm^{-1}; ^{1}H NMR δ 5.55 (2, m), 5.0 (4, m), 3.22 (2, dd, *J* = 7.2, 4.2 Hz), 2.17 (2, m), 1.95–1.30 (6, m), 0.92 (6, d, *J* = 6.8 Hz), 0.85 (6, d, *J* = 6.6 Hz); ^{13}C NMR δ 140.1 (d), 140.0 (d), 116.0 (t), 115.8 (t), 78.7 (d) (2C), 48.6 (d), 48.0 (d), 30.2 (d) (2C), 27.4 (t), 27.36 (t), 20.2 (q) (2C), 15.3 (q) (2C). Anal. Calcd for $C_{16}H_{30}O_2$: C, 75.54; H, 11.89. Found: C, 75.34; H, 11.90.

(5*R,6*R**,9*S**,10*S**)-6,9-Divinyl-5,10-tetradecanediol (6c)** was prepared by addition of **1** to pentanal (**5c**) (1.30 g) (2 h at –85 °C and 2 h at –60 °C). **6c** (obtained as major diastereomer, 92:8) (1.53 g, 72%): oil, IR (film) 3400, 1645, 915 cm^{-1}; ^{1}H NMR δ 5.69–5.44 (2, m), 5.15–5.03 (4, m), 3.61–3.46 (2, m), 2.23–2.06 (4, m), 1.63–1.15 (16, m), 0.9 (6, t, *J* = 6.3 Hz); ^{13}C NMR δ 139.46 (d), 139.4 (d), 116.4 (t), 116.3 (t), 74.0 (d), 73.7 (d), 51.0 (d), 50.5 (d), 33.7 (t), 33.6 (t), 28.0 (t), 27.7 (t), 22.5 (t) (4C), 13.9 (q) (2C). Anal. Calcd for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13. Found: C, 75.34; H, 12.18.

(4*R,5*R**,8*S**,9*S**)-2,11-Dimethyl-5,8-divinyl-3,8-decanediol (6d)** was prepared by addition of **1** to 3-methylbutanal (**5d**) (1.30 g) (3 h at –85 °C and 2 h at –60 °C). **6d** (obtained as major diastereomer, 93:7) (1.63 g, 77%): mp 74 °C; IR (Nujol) 3400, 1645, 915 cm^{-1}; ^{1}H NMR δ 5.66–5.48 (2H, m), 5.14–5.02 (4, m), 3.59–3.48 (2, m), 2.07–2.0 (2, m), 1.86–1.73 (2, m), 1.25 (4, t, *J* = 6.5 Hz), 0.90 (6, t, *J* = 6.95 Hz); ^{13}C NMR δ 139.3 (d), 139.2 (d), 117.46 (t), 117.4 (t), 72.38 (d), 72.2 (d), 51.5 (d), 51.0 (d), 43.3 (d), 43.1 (d), 28.1 (t), 27.5 (t), 24.7 (t) (2C), 24.0 (q), 23.98 (q), 21.6 (q) (2C). Anal. Calcd for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13. Found: C, 76.41; H, 12.16.

(1*S,2*R**,5*S**,6*R**)-1,6-Diphenyl-2,5-divinyl-1,6-hexanediol (6e)** was prepared by addition of **1** to benzaldehyde (**5e**) (1.6 g) (2 h at –90 °C and 16 h at –60 °C). **6e** (obtained as major diastereomer, >98:2) (217 mg, 9%): white crystals, mp 68 °C (CH_2Cl_2); IR (Nujol) 3500–2900, 1955, 1645 cm^{-1}; ^{1}H NMR δ 7.35–7.20 (10, m), 5.56–5.37 (2, m), 5.06–4.87 (4, m), 4.56 (2, d *J* = 5.83 Hz), 2.37–2.15 (2, m), 2.04 (2, br s), 1.67 (1, m), 1.49–1.09 (3, m); ^{13}C NMR δ 142.7 (s), 142.6 (s), 138.4 (d), 138.35 (d), 127.9 (d) (4C), 127.3 (d), 127.28 (d), 126.8 (d) (2C), 126.6 (d) (C), 117.3 (t) (2C), 76.8 (d), 76.6 (d), 51.6 (d), 51.09 (d), 27.7 (t), 26.8 (t). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.71; H, 8.23.

(1*R*,2*S*,3*S*)-2-Phenyl-1,3-divinylcyclopentane (*s-m*-11) and (1*R,3*R**)-2-phenyl-1,3-divinylcyclopentane (*dl*-11)** (obtained as inseparable mixture, 53:47) (2.5 g, 84%); IR (neat) 3080, 3022, 1645, 1605, 915 cm^{-1}; MS (EI) *m/z* (rel intensity) 198 (20), 169 (11), 143 (24), 129 (100), 117 (27), 115 (28), 104 (29), 91 (55); HRMS calcd for $C_{15}H_{18}$ 198.1408, found 198.1411; (*s-m*-11) ^{1}H NMR (400 MHz) δ 7.19 (2, m), 7.11 (3, m), 5.73 (2, ddd, *J* = 17.0, 10.5, 7.6 Hz), 4.82 (4, m), 2.95 (2, m), 2.44 (1, t, *J* = 10.6 Hz), 2.02 (4, m); ^{13}C NMR δ 142.2 (s), 141.1 (d) (2C), 128.2 (d) (2C), 128.0 (d) (2C), 126.2 (d), 113.9 (t) (2C), 58.9 (d), 52.1 (d) (2C), 30.6 (t) (2C); (*dl*-11) ^{1}H NMR (400 MHz) δ 7.19 (2, m), 7.11 (3, m), 5.79 (1, ddd, *J* = 16.9, 10.3, 7.6 Hz), 5.49 (1, ddd, *J* = 17.1, 10.2, 7.8 Hz), 4.99 (1, ddd, *J* = 17.1, 1.6, 1.2 Hz), 4.91 (1, ddd, *J* = 10.2, 1.8, 0.8 Hz), 4.82 (2, m), 3.05 (1, dd, *J* = 10.0, 8.2 Hz), 2.70 (2, m), 1.63 (4, m); ^{13}C NMR δ 142.2 (s), 141.7 (d), 140.2, 129.0 (d) (2C), 127.9 (d) (2C), 125.9 (d), 114.0 (t), 113.8 (t), 55.5 (d), 48.5 (d), 47.3 (d), 31.3 (t), 30.4 (t). Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.55; H, 9.19.

(1*S,2*R**,5*S**,6*R**)-1,6-Bis(*p*-nitrophenyl)-2,5-divinyl-1,6-hexanediol (6f)** was prepared by addition of **1** to *p*-nitrobenzaldehyde (**5f**) (2.26 g) (1 h at –90 °C and 3 h at –60 °C). **6f** (obtained as major diastereomer, >92:8) (1.33 g, 43%): mp 132 °C; IR (Nujol) 3510, 1645, 1610–1600, 920 cm^{-1}; ^{1}H NMR δ 8.15 (4, d, *J* = 8.67 Hz), 7.39 (4, d, *J* = 8.67 Hz), 5.51–5.18 (2, m), 5.12–4.87 (4, m), 4.67 (2, d, *J* = 6.00 Hz), 2.32–2.10 (2, m), 2.10–1.90 (2, m), 1.44–1.02 (4, m); ^{13}C NMR δ 150.1 (s) (2C), 137.5 (d) (2C), 127.5 (d) (4C), 123.4 (d) (4C), 118.6 (t) (2C), 76.2 (d) (2C),

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51.2 (d) (2C), 26.4 (t) (2C). Anal. Calcd for $C_{22}H_{24}N_2O_6$: C, 64.07; H, 5.87; N, 6.79. Found: C, 63.90; H, 5.81; N, 6.79.

(*Z*)-(1*S,2*R**)-1-(*p*-Nitrophenyl)-7-(trimethylsilyl)-2-vinyl-5-hepten-1-ol (7)** (obtained as major diastereomer, >95:5) (550 mg, 11%): IR (neat) 3500, 3085, 3010, 1645, 1610, 1250, 920, 860–840 cm^{-1}; ^1H NMR δ 8.13 (2, d, J = 8.65 Hz), 7.41 (2, d, J = 8.65 Hz), 5.58–5.21 (2, m), 5.15–4.93 (3, m), 4.71 (1, d, J = 5.54 Hz), 2.47–2.24 (2, m), 2.00–1.60 (2, m), 1.58–1.15 (4, m), –0.7 (9, s); ^{13}C NMR δ 150.3 (s), 146.9 (s), 137.6 (d), 127.4 (d) (2C), 126.5 (d), 126.0 (d), 123.0 (d) (2C), 118.2 (t), 76.0 (d), 51.0 (d), 29.2 (t), 24.5 (t), 18.4 (t), –1.9 (q) (3C); ^{29}Si NMR δ/TMS (INEPT sequence) 1.28. Anal. Calcd for $C_{18}H_{27}NO_3Si$: C, 64.83; H, 8.16; N, 4.20. Found: C, 64.93; H, 8.10; N, 4.11.

(1*S,2*R**)-1-(*p*-Nitrophenyl)-2-vinyl-7-hepten-1-ol (8)** (obtained as major diastereomer 80:20) (1.25 g, 32%): IR (neat) 3500, 3085, 1645, 1610, 1000, 920, 860 cm^{-1}; ^1H NMR δ 8.17 (2, d, J = 8.65 Hz), 7.44 (2, d, J = 8.65 Hz), 5.50 (1, ddd, J = 16.93, 10.1, 9.2 Hz), 5.28–4.90 (4, m), 4.73 (1, d, J = 5.70 Hz), 2.42–2.20 (2, m), 2.15–1.95 (2, m), 1.6–1.2 (4, m); minor isomer (in part), 4.56 (1, d, J = 6.98 Hz); ^{13}C NMR δ 150.3 (s), 146.7 (s), 138.4 (d), 137.6 (d), 127.3 (d) (2C), 122.8 (d) (2C), 117.7 (t), 114.3 (t), 75.8 (d), 51.2 (d), 33.4 (t), 28.5 (t), 26.2 (t); minor isomer, 150.3 (s), 146.8 (s), 138.2 (d), 137.4 (d), 127.4 (d), 123.0 (d), 118.9 (t), 114.3 (t), 75.5 (d), 52.1 (d), 33.2 (t), 29.7 (t), 26.03 (t). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.99; H, 7.36; N, 5.36

(3*R,4*R**,7*S**,8*S**)-3,8-Bis(1-methylethyl)-4,7-divinyl-2,9-dioxacyclononanone.** To a solution of **6b** (254 mg, 1 mmol) in Et_2O (25 mL) cooled at 0 °C was added *n*-butyllithium (1.5 N in hexane, 2 mL, 3 mmol). After the solution was stirred for 0.5 h, phosgene (1.93 M in toluene, 0.8 mL, 1.5 mmol) was added. The solution was warmed to room temperature in 16 h and refluxed for 1 h. After usual workup, the crude product was flash chromatographed on silica gel to give **12b** (154 mg, 55%): IR 1778, 1652, 1171 cm^{-1}; ^1H NMR δ 5.40 (2, ddd, J = 17.1, 10.2, 9.5 Hz), 5.15 (2, dd, J = 10.2, 1.6 Hz), 5.10 (2, dd, J = 17.1, 1.6 Hz), 4.71 (2, dd, J = 8.6, 3.9 Hz), 2.31 (2, m), 1.96 (2, sept, d, J = 6.8, 3.9 Hz), 1.4–1.22 (4, m), 0.93 (6, d, J = 6.9 Hz), 0.89 (6, d, J = 6.7 Hz); ^{13}C NMR δ 150.8 (s), 136.6 (d), 118.4 (t), 90.1 (d), 45.6 (d), 29.8 (d), 26.6 (t), 19.7 (q), 15.3 (q); MS m/z $C_{15}H_{25}O_2$ [M^+ – (CH_3 + CO)] calcd 237.1854, obsd 237.186, $C_{16}H_{27}$ [M^+ – (CO_2 + OH)] calcd 219.2113, obsd 219.211, $C_{14}H_{25}O$ [M^+ – (CO_2 + $CH{=}CH_2$)] calcd 209.1905, obsd 209.191. Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.91; H, 10.14.

X-ray Crystallography of $C_{22}H_{26}O_2$ (6e):[24] M_r = 322.45, monoclinic, $P21/c$, a = 12.200(4), b = 5.309(3), c = 14.732(3) Å, β = 101.15(2)°, V = 936.1(8) Å^{-3}, Z = 2, D_x = 1.144 mg·m^{-3}, λ(Mo Kα) = 0.70926 Å, μ = 0.67 cm^{-1}, $F(000)$ = 348, T = 293 K, final R = 0.043 for 670 observations.

A crystal of **6e** of dimensions 0.1 × 0.15 × 0.3 mm was studied on an automatic diffractometer (CAD4 ENRAF-NONIUS) with graphite monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max}$ = 50°, scan $\omega/2\theta$ = 1, t_{max} = 60 s, range hkl h 0.17 K 0.6 L –14.14, intensity controls without appreciable decay (0.1%)) give 1930 reflections from which 670 were independent (R_{int} = 0.017) with $I > 3\sigma(I)$. After Lorenz and polarization corrections, the structure was solved by direct methods which reveal all the non-hydrogen atoms. After isotropic (R = 0.11) and then anisotropic refinement (R = 0.088), the hydrogen atoms were found with a Fourier difference (between 0.42 and 0.15 e Å^{-3}). The whole structure was refined by the full-matrix least-square techniques (use of F magnitude; x, y, z, β_{ij} for C and O atoms and s, y, z for H atoms; 149 variables and 670 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting R = 0.044, R_w = 0.043, and S_w = 0.75 (residual $\Delta\rho \leq 0.18$ eÅ^{-3}). All the calculations were performed on Digital Micro VAX 3100 computer with the MOLEN package (Enraf-Nonius, 1990).

Acknowledgment. We thank Dr. I. D. R. Stevens (University of Southhampton, U.K.) for critical reading of the manuscript. We are indebted to Dr. R. Faure for his assistance in NMR measurements.

(24) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.