$C_{18}H_{27}O_2Si$ m/z 303.1780, found m/z 303.1758.

Preparation of (*E*,4*S,5*R**)-4-[(Methanesulfonyl)oxy]-5-[(*tert*-butyldimethylsilyl)oxy]-2-hexenenitrile (9).** As a phosphonate reagent, $(EtO)_2P(O)CH_2CN$ was used: colorless oil; ^1H NMR ($CDCl_3$) δ 0.10 (s, 3 H), 0.10 (s, 3 H), 0.90 (s, 9 H), 1.18 (d, J = 6.5 Hz, 3 H), 3.09 (s, 3 H), 4.05 (dq, J = 6.5 and 3.7 Hz, 1 H), 5.01 (ddd, J = 5.6, 3.7, and 1.7 Hz, 1 H), 5.73 (dd, J = 16.1 and 1.7 Hz, 1 H), 6.71 (dd, J = 16.1 and 5.6 Hz, 1 H); IR ($CHCl_3$) 3030, 2965, 2940, 2870, 2245, 1475, 1465, 1365, 1355, 1260, 1185, 1120, 980, 945, 850, cm^{-1}; exact MS (EI) calcd for $(M - CH_3)^{+}$ $C_{12}H_{22}NO_4SiS$ m/z 304.1039, found m/z 304.1034.

(*E*,2*S,5*R*)-2-Methyl-5-[(*tert*-butyldimethylsilyl)oxy]-3-hexenenitrile (10):** colorless oil; ^1H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.90 (s, 9 H), 1.21 (d, J = 6.5 Hz, 3 H), 1.40 (d, J = 7.2 Hz, 3 H), 3.24–3.37 (m, 1 H), 4.27–4.38 (m, 1 H), 5.55 (ddd, J = 15.0, 6.0, and 1.6 Hz, 1 H), 5.84 (ddd, J = 15.0, 4.8, and 1.5 Hz, 1 H); IR (CCl_4) 2960, 2930, 2850, 2230, 1725, 1470, 1460, 1368, 1358, 1250, 1148, 1090, 1050, 968, and 835 cm^{-1}; exact MS (EI) calcd for M^+ $C_{13}H_{25}NOSi$ m/z 239.1705, found m/z 239.1707.

Registry No. 1, 129389-01-1; 2 (R = Me), 138126-75-7; 2 (R = *n*-Bu), 138126-76-8; 3, 129389-00-0; 4 (R = Me), 138126-77-9; 4 (R = *n*-Bu), 138126-78-0; 5, 138009-29-7; 6, 138009-30-0; 7, 138009-31-1; 8, 138009-32-2; 9, 138009-33-3; 10, 138009-34-4; 11, 138009-35-5; 12, 81028-12-8; 13, 138009-36-6; $ZnCl_2$, 7646-85-7; CuCN, 544-92-3; MeLi, 917-54-4; *n*-BuLi, 109-72-8; MeI, 74-88-4; Zn, 7440-66-6; Me_2CuLi, 15681-48-8.

Supplementary Material Available: Synthetic methods and spectral data for 1–11 (13 pages). Ordering information is given on any current masthead page.

Stereoselective Dimerizations of Arene-*cis*-diol Acetonides Derived from the Oxidation of Halobenzenes by *Pseudomonas putida*: Absolute Configuration of the Adducts by X-ray Crystallography

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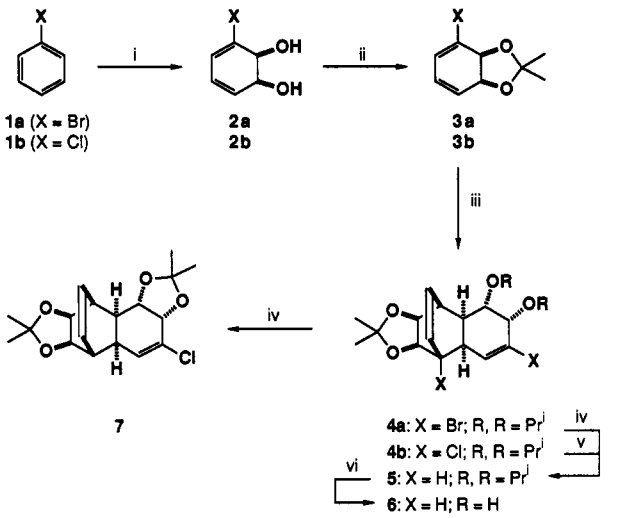
The microbial oxidation of aromatic compounds to the corresponding arene-*cis*-diol metabolites by mutant strains of *Pseudomonas putida* (e.g. 1 → 2) has been the subject of considerable biochemical research since its introduction in 1970 by Gibson et al.[1] The high degree of stereospecificity, substrate variability, and procedural ease inherent with these microbial oxidations have made the diols especially attractive in recent years as starting materials in enantiocontrolled total synthesis.[2] This has subsequently led to their commercial availability as chiral synthons.[3] In response to this wave of interest, Boyd and co-workers have recently developed a general method for determining absolute configuration and optical purity of *cis*-diol metabolites.[4]

Synthetic applications involving *cis*-diol metabolites often require protection of the hydroxyl groups in the form of an acetonide. We wish to report that halogenated arene-*cis*-diol acetonides (3) dimerize in a completely stereoselective fashion to highly stable crystalline dimers (4) (Scheme I).[5] In addition, the absolute configuration of the bromo dimer (4a) was established by X-ray crystallography which confirmed independently the absolute configuration of the *P. putida* 39-D metabolite 2a of bromobenzene. The absolute configuration of the chloro dimer (4b) was established by chemical correlation which involved reduction of both 4a and 4b to the nonhalogenated adduct 5, followed by partial deprotection to the diol 6.

Scheme I[a]



[a] (i) *P. putida* 39-D; (ii) DMP, pTsOH (cat.), acetone; (iii) neat, 0 °C → rt; (iv) Bu_3SnH, AIBN, tol., Δ; (v) Na^0, EtOH, Δ; (vi) HOAc, H_2O, rt.

Table I. Reaction Conditions and Yields for the Dimerizations of 3 to 4

acetonide	X	reaction conditions	% yield of 4[a]
3a	Br	neat, 0 °C, 15 d	32 (61)
3b	Cl	neat, 0 °C, 23 d	49 (51)
3a	Br	neat, rt 8 d	80
3b	Cl	neat, rt, 8 d	71
3a	Br	$CDCl_3$, 60 °C, 8 d (sealed tube)	70[b]
3a	Br	$CDCl_3$, 100 °C, 2 d (sealed tube)	–[c]
3b	Cl	$CDCl_3$, 100 °C, 6 d (sealed tube)	>95[b]

[a] Isolated yield of 4, percent recovery of unreacted 3 from chromatography is given in parentheses. [b] Determined from the ^1H NMR spectra. [c] Starting material underwent significant aromatization.

Reaction conditions and yields for the dimerizations of 3 to 4 are provided in Table I. The acetonide 3a of bro-

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(1) Gibson, D. T.; Hensley, M.; Yoshioka, H.; Mabry, T. J. *Biochemistry* **1970**, *9*, 1626.

(2) (a) Hudlicky, T.; Luna, H.; Price, J. D.; Rulin, F. *Tetrahedron Lett.* **1989**, *30*, 4053. (b) Hudlicky, T.; Seoane, G.; Pettus, T. *J. Org. Chem.* **1989**, *54*, 4239. (c) Hudlicky, T.; Luna, H.; Price, J. D.; Rulin, F. *J. Org. Chem.* **1990**, *55*, 4683. (d) Hudlicky, T.; Price, J. D. *Synlett* **1990**, 159. (e) Hudlicky, T.; Rulin, F.; Tsunoda, T.; Price J. D. *J. Am. Chem. Soc.* **1990**, *112*, 9439. (f) Ley, S. V. *Pure Appl. Chem.* **1990**, *62*, 2031. (g) Ley, S. V.; Redgrave, A. J. *Synlett* **1990**, *7*, 393. (h) Carless, H. A. J.; Billinge, J. R.; Oak, O. Z. *Tetrahedron Lett.* **1989**, *30*, 3113. (i) Carless, H. A. J.; Oak, O. Z. *J. Chem. Soc., Chem. Commun.* **1991**, 61.

(3) A variety of arene-*cis*-diols are available in multigram quantities from Genencor International, Inc., Rochester, NY, and ICI Fine Chemicals, P.O. Box 42 Hexagon House, Blackley, Manchester, M9 3DA, England.

(4) Boyd, D. R.; Dorrity, M. R. J.; Hand, M. V.; Malone, J. F.; Sharma, N. D.; Dalton, H.; Gray, D. J.; Sheldrake, G. N. *J. Am. Chem. Soc.* **1991**, *113*, 666.

(5) A similar dimerization involving the acetonide of trifluorotoluenediol has been described (e.g. 3 → 4; X = CF_3). Our crystal structure of 4a concurs with the stereochemistry assigned to the trifluoro dimer which was deduced using a variety of NMR methods, see: Pittol, C. A.; Pryce, R. J.; Roberts, S. M.; Ryback, G.; Sik, V.; Williams, J. O. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1160.

0022-3263/92/1957-1026$03.00/0

mobenzenediol was prepared in the usual fashion from **2a** and dimethoxypropane (DMP) and stored as the neat oil under argon at 0 °C for ca. 2 weeks. TLC analysis of the resulting viscous oil revealed, in addition to **3a**, a slower eluting, non-UV-active spot. Purification by flash chromatography provided a crystalline substance which by ^1H NMR appeared to be a single diastereomer. Close inspection of the ^1H NMR spectrum suggested a dimer produced via a Diels–Alder reaction in which the unsubstituted double bond of **3a** served as the dienophile. This conclusion was supported by ^{13}C NMR analysis. Recrystallization and subsequent X-ray studies (through analysis of anomalous dispersion) established the absolute configuration of **4a** as that shown in Scheme I. Although the isolated yield of **4a** was only 32%, it was the only product detected (61% recovery of **3a**), indicating a completely stereoselective dimerization. This result, together with earlier synthetic ventures,[2e] firmly establishes the absolute configuration of **2a** obtained from the *Pp*-39D oxidation of bromobenzene as 2*S*,3*S*, which to our knowledge has not been previously reported. Similar results were obtained with the acetonide **3b** of chlorobenzenediol at 0 °C, whose absolute configuration is known.[4]

We have found that the most convenient method of dimerization simply involves storing the acetonides (**3**) as neat oils at room temperature under argon for about 1 week. Residual acetonide is then removed under high vacuum and the resulting material recrystallized from a mixture of EtOAc and hexanes. Employing this method, **4a** and **4b** were isolated in 80 and 71% yields, respectively.

In order to unambiguously establish the absolute configuration of **4b**, both **4a** and **4b** were converted in two steps to the nonhalogenated *cis*-diol **6**. The reduction of **4a** with tributyltin hydride (Bu_3SnH) proceeded smoothly in refluxing toluene to provide **5** in 91% isolated yield. Interestingly, similar treatment of the chloro dimer **4b** removed *only* the bridgehead chlorine atom, and the resulting vinylic chloride (**7**) was obtained in near quantitative yield. Conversely, exposing **4b** to sodium metal in refluxing ethanol[6] accomplished the desired conversion to **5** in 48% isolated yield. Unfortunately, the dehalogenated dimer **5** produced only the slightest optical rotation; consequently, an accurate comparison of optical activities of **5** obtained from both **4a** and **4b** was not possible. For this reason, **5** was partially deprotected to the *cis*-diol (**6**) which was strongly levarotory, allowing a better comparison of optical activities. The specific rotations of **6** obtained from **4a** and **4b** were −78° and −83°, respectively.

The facial selectivity[7] observed in these dimerizations is best explained by steric effects. Assuming a concerted mechanism, the transition states leading to **4a** and **4b** provide for a minimum of steric interactions. The regioselectivity in the reaction appears to be consistent with inverse electron demand since the double bond bearing the electron-withdrawing group (i.e. the halogen atom) does not serve as the dienophile in these instances.

Owing to the remarkable stereoselectivity observed for the dimerizations of **3a** and **3b** as neat oils at lower temperatures, it was of interest to examine the process in solution under thermal conditions. A ca. 0.3 M solution of **3a** in $CDCl_3$ was heated to 100 °C in a sealed NMR tube and analyzed periodically by ^1H NMR. Under these conditions, **3a** underwent significant aromatization with concomitant acetone production after a few days. Storing the $CDCl_3$ over Na_2CO_3 and/or filtration through alumina did not alleviate this problem. Performing the dimerization of **3a** at 60 °C in $CDCl_3$ resulted in considerably less aromatized starting material, and under these conditions **4a** was formed in ca. 70% yield after 8 d. In contrast, the acetonide **3b** dimerized almost *quantitatively* to **4b** in $CDCl_3$ at 100 °C over a period of 6 d without aromatization. This result is remarkable when considering the stereoselectivity observed, the susceptibility of the starting materials to aromatization, and the low reactivity of the acting dienophiles.

In summary, we have demonstrated a general property of halogenated arene-*cis*-diol acetonides to dimerize under relatively mild conditions with complete stereoselectivity. Since the conversion of arene-*cis*-diols to their acetonides is a common method of protection, researchers should take note of this possible dimerization. On the other hand, the resulting dimers may be obtained in good yield and are stable, crystalline substances suitable for X-ray analysis. Particularly in the case of new *cis*-diol metabolites isolated in future endeavors, this acetonide dimerization may prove useful as a simple means of obtaining stable dimeric materials more amenable to certain types of characterization. It may also be interesting to see what use structures of types **4–7** bring in designing chiral catalysts and auxiliaries. Such efforts are projected for the future.

Experimental Section

All NMR spectra were measured in $CDCl_3$ solutions with reference to $CHCl_3$ (δ 7.24) or TMS (δ 0.0) as internal standards for ^1H NMR and the $CDCl_3$ triplet (δ 77.0) for ^{13}C NMR. Carbon multiplicities were determined from DEPT experiments. Coupling constants are given in hertz. Infrared (IR) spectra were measured as KBr pellets unless noted otherwise. All elemental analyses were performed by Atlantic Microlabs, Norcross, GA. Chromatographic separations were performed on Merck silica gel 60 (230–400 mesh).

(1*S*,2*S*,5*S*,6*S*,7*R*,8*S*,9*S*,10*S*)-1,4-Dibromo-5,6:9,10-bis(isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-3,11-diene (4a). Acetonide **3a** (1.57 g, 6.79 mmol) was refrigerated as the neat oil under argon at ca. 0 °C for 15 d. The resulting viscous oil was purified by flash chromatography on silica gel, eluting with 5% EtOAc/hexanes to provide in the front-running fractions recovered **3a** (0.961 g, 4.16 mmol, 61% recovery) followed by the slower eluting **4a**. Recrystallization of the latter from a mixture of EtOAc/hexanes provided pure **4a** as a white crystalline solid (0.510 g, 1.10 mmol, 32% yield): mp 192–193 °C; $[\alpha]_D$ = +105.6° (*c* 1.70, $CHCl_3$); IR ν 3040, 2980, 2860, 1365, 1270, 1210, 1160 cm^{-1}; ^1H NMR (270 MHz) δ 6.49 (1 H, d, *J* = 3.8), 6.09 (1 H, d, *J* = 8.6), 5.88 (1 H, dd, *J* = 8.6, 6.3), 4.37 (2 H, br s), 4.20 (1 H, d, *J* = 4.6), 4.17 (1 H, br d, *J* = 4.6), 2.87 (1 H, br d, *J* = 6.3), 2.72 (1 H, dd, *J* = 8.9, 3.8), 2.43 (1 H, d, *J* = 8.9), 1.40 (3 H, s), 1.35 (3 H, s), 1.34 (3 H, s), 1.31 (3 H, s); ^{13}C NMR δ 136.3 (CH), 129.6 (CH), 128.4 (CH), 125.3 (C), 109.8 (C), 108.8 (C), 83.4 (CH), 79.1 (CH), 79.0 (CH), 73.4 (CH), 66.6 (C), 43.9 (CH), 38.8 (CH), 35.4 (CH), 27.7 (CH_3), 26.6 (CH_3), 25.4 (CH_3), 25.0 (CH_3). Anal. Calcd for $C_{18}H_{22}Br_2O_4$: C, 46.78; H, 4.80. Found: C, 46.88; H, 4.81.

(1*S*,2*S*,5*S*,6*S*,7*R*,8*S*,9*S*,10*S*)-1,4-Dichloro-5,6:9,10-bis(isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-3,11-diene (4b). The acetonide **3b** (0.150 g, 0.201 mmol) was treated as described above for 23 d. Purification by flash chromatography on silica gel eluting with 30% EtOAc/hexanes provided pure **4b** as a white crystalline solid (0.073 g, 0.196 mmol, 49% yield): mp 148–149 °C; $[\alpha]_D$ = +84.0° (*c* 0.35, $CHCl_3$); IR ν 3070, 2981, 1660, 1378, 1217, 1087 cm^{-1}; ^1H NMR δ 6.16 (1 H, d, *J* = 3.9), 5.97 (2 H, m), 4.39 (1 H, dd, *J* = 7.2, 3.4), 4.28 (1 H, d, *J* = 7.2), 4.21 (1 H, d, *J* = 3.9), 4.14 (1 H, d, *J* = 4.7), 2.88 (1 H, m), 2.71 (1 H, ddd, *J* = 8.9, 3.9, 1.6), 2.41 (1 H, d, *J* = 9.0), 1.38 (3 H, s), 1.35 (6 H, s), 1.30 (3 H, s); ^{13}C NMR δ 135.4 (CH), 133.3 (C), 128.1 (CH), 124.3 (CH), 110.1 (C), 108.9 (C), 82.9 (CH), 79.0 (CH), 78.9 (CH), 72.4 (CH), 42.7 (CH), 39.1 (CH), 35.1 (CH), 27.7 (CH_3), 26.6 (CH_3), 25.4 (CH_3), 25.1 (CH_3). Anal. Calcd for $C_{18}H_{22}Cl_2O_4$: C, 57.92; H, 5.94. Found: C, 57.98; H, 5.98.

(6) Lap, B. V.; Paddon-Row, M. N. *J. Org. Chem.* **1979**, *44*, 4979.
(7) Facial selectivity in the Diels–Alder reaction has received considerable attention recently, see: Tsuji, T.; Ohkita, M.; Nishida, S. *J. Org. Chem.* **1991**, *56*, 997 and references cited therein.

(1*S*,2*S*,3*S*,4*R*,7*S*,8*R*,9*R*,10*S*)-3,4:9,10-Bis(isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-5,11-diene (5) from 4a. To a solution of **4a** (0.119 g, 0.257 mmol) in toluene (2.5 mL) was added Bu_3SnH (0.600 g, 2.06 mmol) followed by AIBN (0.042 g, 0.256 mmol), and the solution was refluxed under an argon atmosphere for 26 h. The reaction mixture was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel eluting with 15% EtOAc/hexanes to provide pure **5** as white crystals (0.071 g, 0.233 mmol, 91% yield): mp 150–151 °C; ^1H NMR δ 5.96 (2 H, m), 5.58 (1 H, ddd, J = 10.2, 3.6, 1.4), 5.48 (1 H, ddd, J = 10.2, 3.0, 1.5), 4.30 (1 H, dd, J = 7.3, 3.1), 4.25 (1 H, dd, J = 7.3, 3.0), 4.18 (1 H, ddd, J = 4.9, 3.6, 1.4), 4.13 (1 H, br d, J = 4.9), 2.85 (2 H, m), 2.34 (1 H, m), 2.20 (1 H, br d, J = 9.0), 1.33 (3 H, s), 1.31 (3 H, s), 1.29 (3 H, s), 1.26 (3 H, s); ^{13}C NMR δ 132.4 (CH), 129.3 (CH), 128.8 (CH), 126.6 (CH), 108.6 (C), 107.6 (C), 78.6 (CH), 78.4 (CH), 77.6 (CH), 70.9 (CH), 41.0 (CH), 40.7 (CH), 34.3 (CH), 33.1 (CH), 28.3 (CH_3), 26.8 (CH_3), 25.4 (CH_3), 25.0 (CH_3). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 70.89; H, 8.02.

(1*R*,2*S*,5*S*,6*S*,7*S*,8*S*,9*S*,10*R*)-4-Chloro-5,6:9,10-bis(isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-3,11-diene (7) from 4b. To a solution of **4b** (72.3 mg, 0.194 mmol) and AIBN (cat. quantity) in toluene (3 mL) was added Bu_3SnH (225 mg, 0.775 mmol), and the reaction mixture was refluxed under an argon atmosphere for 3 h. The mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel eluting with 20% EtOAc/hexanes to afford pure **7** as white crystals (65.5 mg, 0.194 mmol, 100% yield): mp 148–150 °C; $[\alpha]_D$ = +114° (c 0.6, $CHCl_3$); IR ν 3040, 2981, 1664, 1371, 1208, 1062, 876 cm^{-1}; ^1H NMR δ 6.03 (2 H, m), 5.71 (1 H, d, J = 4.3), 4.27 (1 H, m), 4.14 (1 H, d, J = 4.6), 2.86 (2 H, m), 2.53 (1 H, m), 2.23 (1 H, d, J = 9.0), 1.37 (3 H, s), 1.34 (3 H, s), 1.29 (3 H, s), 1.25 (3 H, s); ^{13}C NMR δ 132.5 (CH), 131.3 (CH), 128.8 (C), 127.9 (CH), 108.9 (C), 108.5 (C), 79.5 (CH), 78.6 (CH), 77.9 (CH), 72.7 (CH), 41.2 (CH), 40.4 (CH), 35.7 (CH), 34.3 (CH), 27.8 (CH_3), 26.6 (CH_3), 25.4 (CH_3), 25.0 (CH_3). Anal. Calcd for $C_{18}H_{23}ClO_4$: C, 63.81; H, 6.84. Found: C, 63.84; H, 6.89.

(1*S*,2*S*,3*S*,4*R*,7*S*,8*R*,9*R*,10*S*)-3,4:9,10-Bis(isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-5,11-diene (5) from 4b. A solution of **4b** (80 mg, 0.214 mmol) in absolute ethanol (2 ml) was heated to reflux, and finely divided sodium metal (130 mg, 5.65 mmol) was added in ca. 10-mg portions over a period of 1.25 h while monitoring the progress of the reaction by TLC. When the reaction was complete, the mixture was cooled to rt and quenched with H_2O (0.5 mL). The ethanol was removed in vacuo, and the aqueous mixture was extracted with CH_2Cl_2 (4 × 8 mL). The combined organic layers were washed with H_2O (1 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to provide 66 mg of crude brown oil. Flash chromatography through a small pipet eluting with a solvent gradient of 0 → 25% EtOAc/hexanes provided pure **5** as a white solid (31 mg, 0.101 mmol, 48% yield). The spectral data were identical to that shown for **5** above.

(1*S*,2*S*,3*S*,4*R*,7*S*,8*R*,9*R*,10*S*)-9,10-(Isopropylidenedioxy)tricyclo[6.2.2.0]dodeca-5,11-diene-3,4-diol (6). A solution of **5** (28 mg, 0.092 mmol) in glacial acetic acid (1 mL) and H_2O (0.2 mL) was stirred at rt for 18 h. The solution was saturated with NaCl and extracted with EtOAc (4 × 2 mL). The combined organic layers were washed with saturated $NaHCO_3$ (3 × 1 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was recrystallized from a mixture of EtOAc/hexanes to provide the pure diol (**6**) as a white crystalline solid (15 mg, 0.0567 mmol, 63% yield): mp 123–125 °C; $[\alpha]_D$ = −78° synthesized from **4a** (c 0.72, $CHCl_3$), $[\alpha]_D$ = −83° synthesized from **4b** (c 0.93, $CHCl_3$); IR ($CHCl_3$) ν 3580, 3440, 3005, 2960, 2920, 1380, 1205, 1065 cm^{-1}; ^1H NMR δ 6.05 (2 H, m), 5.72 (2 H, m), 4.26 (2 H, m), 4.04 (1 H, br s), 3.54 (1 H, br s), 3.05 (1 H, m), 2.84 (1 H, m), 2.35 (1 H, br d, J = 8.8), 2.01 (3 H, m), 1.31 (3 H, s), 1.26 (3 H, s); ^{13}C NMR δ 134.1 (CH), 130.8 (CH), 130.7 (CH), 127.3 (CH), 108.6 (C), 78.7 (CH), 78.6 (CH), 71.7 (CH), 66.6 (CH), 40.4 (CH), 38.5 (CH), 38.0 (CH), 35.1 (CH), 25.4 (CH_3), 25.0 (CH_3).

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Note Added in Proof. A paper describing the dimer **4a** appeared while this manuscript was being processed: Ley, S. V.; Redgrave, A. J.; Taylor, S. C.; Abmed, S.; Ribbons, D. W. *Synlett* **1991**, 741.

Registry No. 2a, 130792-45-9; **3a**, 130669-75-9; **3b**, 127666-06-2; **4a**, 137769-14-3; **4b**, 137792-30-4; **5**, 137769-15-4; **6**, 137792-31-5; **7**, 137769-16-5.

Supplementary Material Available: X-ray crystallographic data for compound **4a** and ^1H and ^{13}C NMR spectra for compounds **4a**, **4b**, **5**, **6**, and **7** (17 pages). Ordering information is given on any current masthead page.

Reductive Cleavage of *tert*-Butyldimethylsilyl Ethers by Diisobutylaluminum Hydride

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The utility of the *tert*-butyldimethylsilyl (Tbs) group for the protection of hydroxyl groups[1,2] has been enhanced by the availability of diverse methods for its introduction[1,3] and removal (especially fluoride ion,[1] aqueous acid,[1,2] and aqueous HF–CH_3CN[4]). We report herein a new method for the cleavage of Tbs ethers under reductive and near-neutral conditions using diisobutylaluminum hydride (DIBAL-H). In the original research on protection of the hydroxyl function by Tbs it was found that the conversion of a γ-lactone to the corresponding lactol could be carried out selectively with DIBAL-H (1.2 equiv) in toluene at −78 °C in the presence of the Tbs ether function which remained unchanged,[1] and many instances of such reactions are now known. Nonetheless, Tbs ethers react with DIBAL-H in methylene chloride solution at 23 °C in 1–2 h to yield desilylated alcohols (1) according to the following equation.

$$\underset{\mathbf{1}}{\mathrm{ROSiMe_2}t\text{-Bu}} + i\text{-Bu}_2\mathrm{AlH} \rightarrow \underset{\mathbf{3}}{\mathrm{ROAl}i\text{-Bu}_2} + \underset{\mathbf{2}}{\mathrm{HSiMe_2}t\text{-Bu}}$$

The formation of *tert*-butyldimethylsilane (**2**) was established by 500-MHz ^1H NMR analysis of the cleavage reaction in carbon tetrachloride or deuteriochloroform solution which revealed the simultaneous development of peaks due to **2**[5] and **3**. The cleavage reaction was clean and complete with a series of test cases which gave pure alcohols simply by extractive isolation in the indicated isolated yields (in parentheses): 1-hexanol (93%), benzyl alcohol (91%), phenol (84%), *trans*-4-*tert*-butylcyclohexanol (87%). The mildness of the method is indicated by the deprotection of the chiral 1,2-propadienyl ether **4**

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