Stereoselective hydrogenation of lignin degradation model compounds

Thomas Q. Hu, Brian R. James, Steven J. Rettig, and Chung-Li Lee

Abstract: Di-μ-chloro-bis(η^4-1,5-hexadiene)dirhodium(I) in a two-phase hexane–aqueous medium catalyzes the diastereoselective H_2-hydrogenation of lignin degradation model compounds 4-propylphenol, 2-methoxy-4-propylphenol, and 2,6-dimethoxy-4-propylphenol. The all-*cis* diastereomer is obtained selectively when the phenolic hydroxy group is protected as a methyl ether or when a model compound possessing two methoxy substituents adjacent to the phenolic hydroxy group is used. The relative stereochemistries of the hydrogenated products are established by X-ray crystal structure analysis and (or) ^{1}H NMR.

Key words: catalytic hydrogenation, diastereomer, lignin degradation model compounds, stereoselective, X-ray crystal structure.

Résumé : Dans un milieu aqueux à deux phases avec de l'hexane, le di-μ-chlorobis(η^4-hexa-1,5-diène)dirhodium(I) catalyse l'hydrogénation diastéréosélective des composés modèles de la dégradation de la lignine, 4-propylphénol, 2-méthoxy-4-propylphénol et 2,6-diméthoxy 4-propylphénol. On obtient sélectivement le diastéréomère complètement *cis* lorsque le groupe hydroxyle phénolique est protégé sous la forme d'éther méthylique ou lorsqu'on utilise un composé modèle possédant deux substituants méthoxy dans les positions adjacentes du groupe hydroxyle phénolique. On a déterminé les stéréochimies relatives des produits d'hydrogénation par le biais de la diffraction des rayons X et (ou) de la RMN du ^{1}H.

Mots clés : hydrogénation, diastéréomère, composés modèles de dégradation de la lignine, stéréosélective, structure cristalline par diffraction des rayons X.

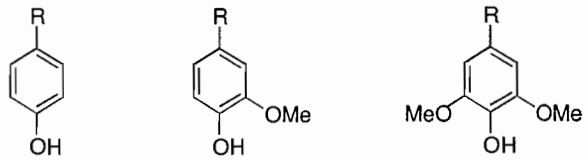
[Traduit par la rédaction]

Introduction

Lignin, a plant constituent, is the second most abundant biopolymer on earth. The biosphere is estimated to contain 3×10^{11} metric tons of lignin with an annual biosynthesis rate of approximately 2×10^{10} tons (1, 2). Every year more than 50 million tons of lignin are produced as the by-products from the chemical pulping of wood at pulp mills worldwide (3). The lignin so obtained has been used mainly as a low-grade fuel for the pulping process (4). Despite extensive research on the conversion of lignin into valuable fine chemicals over the past 20 years or so, only a few systems have been successfully developed and commercialized. One of these commercialized fine chemicals is vanillin, a common flavoring additive in foods and drinks (5).

The major impediments to the exploitation of lignin as a source of fine chemicals are the difficulties involved in separating a mixture of lignin degradation products and the low commercial values of the isolated products. Degradation of lignin obtained from the chemical pulping of wood via neutral or alkaline hydrogenolysis gives 4-substituted-phenols (**1**), 2-methoxy-4-substituted-phenols (**2**) and 2,6-dimethoxy-4-substituted-phenols (**3**) (Scheme 1) in various yields (6–9).

Scheme 1. Products from the degradation of lignin via hydrogenolysis (R = $CH_2CH_2CH_3$, $CH_2CH_2CH_2OH$, CH_2CH_2COOH, CH_2CH_3, CH_2CH_2OH, CH_2COOH, CH_3, COOH, H) (6).



Since the late 1960s sporadic attempts have been made to convert these aromatic compounds into cyclohexanol derivatives via catalytic hydrogenation (10–12). Typically, the reaction was carried out either at high temperature (>200°C) under high pressure (>1000 psi H_2 (1 psi = 6.9 kPa)) (10) or in the presence of strong acid or base (11, 12). Under such reaction conditions, the hydrogenation of the aromatic rings was accompanied by hydrogenolysis of the substituent side chains, giving a multitude of products (10–12). In addition, the hydrogenation was not stereoselective, further complicating the problems of product isolation and development.

In this paper we present the ^{1}H NMR spectroscopic and X-ray crystallographic evidence for the stereoselective hydrogenation of a number of lignin degradation model compounds catalyzed by di-μ-chloro-bis(η^4-1,5-hexadiene)dirhodium(I), $[(1,5\text{-}C_6H_{10})RhCl]_2$. This catalyst was previously used by others for the hydrogenation of carbonyl and simple aromatic

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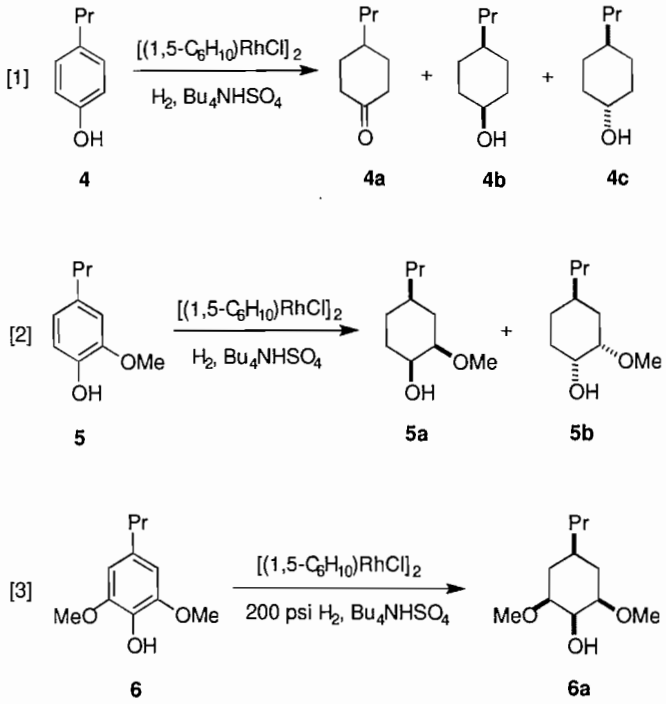
compounds in a two-phase hexane–aqueous medium at room temperature under 1 atm H_2 (101.3 kPa) (13, 14). The extremely mild reaction conditions prompted us to evaluate its potential in the stereoselective (*cis* vs. *trans* diastereomer) hydrogenation of lignin degradation model compounds. We have reported preliminary work on the catalytic hydrogenation of such model compounds using this Rh system; the aim of this work was to inhibit light-induced yellowing of lignin-rich mechanical wood pulp and paper (15).

Results and discussion

Propylphenol (**4**), 2-methoxy-4-propylphenol (**5**), and 2,6-dimethoxy-4-propylphenol (**6**) were selected as the model substrates (16). The catalytic hydrogenation reactions of these three model compounds are summarized in eqs. [1]–[3] (Pr = *n*-propyl).



Hydrogenation of **4** (50 h at ambient conditions in a two-phase medium with Bu_4NHSO_4 as a phase-transfer agent) afforded 4-propylcyclohexanone (**4a**), *cis*-4-propylcyclohexanol (**4b**), and *trans*-4-propylcyclohexanol (**4c**) in a 1:6:2 ratio with an 89% isolated yield. With a longer reaction time, **4a** was further hydrogenated to **4b** and **4c**. The diastereoselectivity of the hydrogenation was 3:1 in favor of **4b** (Table 1). The presence of a methoxy substituent adjacent to the phenolic hydroxyl group increases the diastereoselectivity of the reaction: hydrogenation of **5** afforded predominantly *cis*-2-methoxy-*cis*-4-propylcyclohexanol (**5a**) and *cis*-2-methoxy-*trans*-4-propylcyclohexanol (**5b**) in a 6:1 ratio, while the hydrogenation of **6** gave exclusively the all-*cis* diastereomer (**6a**) (100% diastereoselectivity) (Table 1). Hydrogenation of **6** was carried out under 200 psi H_2 because the reaction was extremely slow under 1 atm H_2.

The relative stereochemistries of **4b** and **4c** were established by ^{1}H NMR. **4b** has a multiplet signal (m) centered at δ 3.94 ascribable to the equatorial methine proton adjacent to the OH group in the *cis* diastereomer, while **4c** has a signal centered at

Table 1. Diastereoselectivity of the hydrogenation of lignin degradation model compounds.

Model compound	Major diastereomer (%)
4	**4b** (75)
5	**5a** (86)
6	**6a** (~100)

Fig. 1. ^{1}H NMR assignment of the relative stereochemistries of **4b** and **4c**.

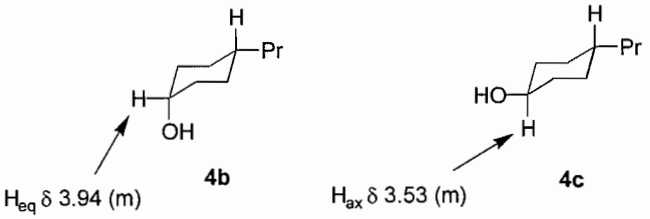
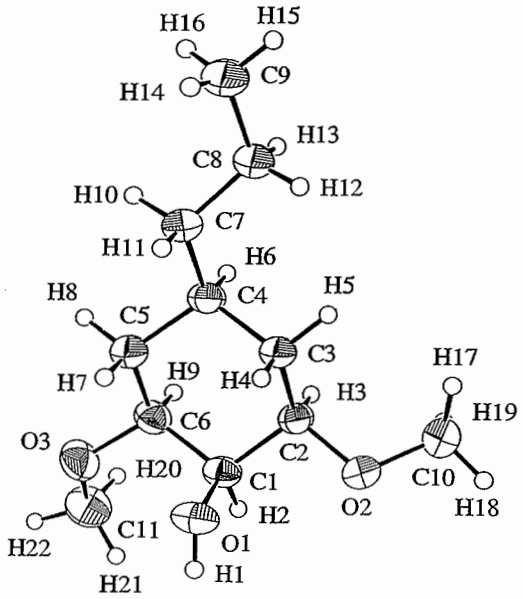


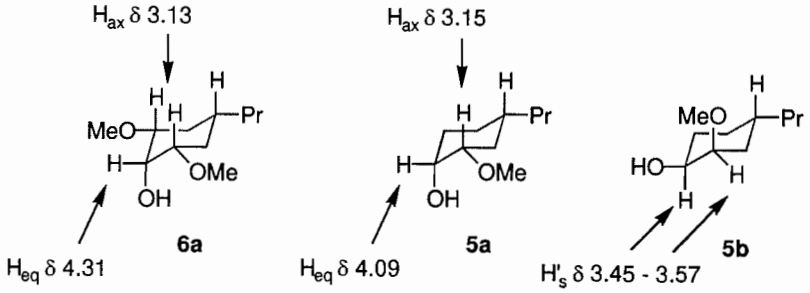
Fig. 2. ORTEP diagram of **6a**, showing 33% probability thermal ellipsoids.



δ 3.53 (m) ascribable to the axial methine proton adjacent to the OH group in the *trans* diastereomer (Fig. 1) (17).

The relative stereochemistry of **6a** was established by X-ray crystal structure analysis, the ORTEP diagram being given in Figure 2. The atomic coordinates and equivalent isotropic thermal parameters for the C and O atoms are given in Table 2. The two OMe substituents are both *cis* to the OH group, with the torsion angles involving the OMe and the OH oxygens (O(1)-C(1)-C(2)-O(2) and O(1)-C(1)-C(6)-O(3)) being close to *gauche* (61.0° and −57.1°, respectively), while the torsion angles involving the hydrogens at the OMe carbon atoms and the OH oxygen (O(1)-C(1)-C(2)-H(3) and O(1)-C(1)-C(6)-H(9)) are close to *trans* (175° and −176°, respectively). The Pr substituent is *cis* to both OMe groups and thus *cis* to the OH group; H(6) and H(3) are mutually *cis*, and are both *trans* to

Fig. 3. ^{1}H NMR assignment of the relative stereochemistries of **5a** and **5b**.



Scheme 2. Enol–keto tautomerization in the formation of *trans*-4-propylcyclohexanol (**4c**).

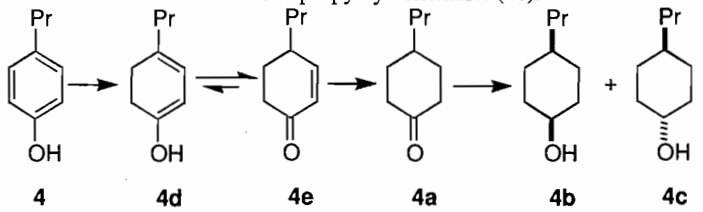


Table 2. Oxygen and carbon atomic coordinates and B_{eq} with estimated standard deviations in parentheses.

Atom	*x*	*y*	*z*	B_{eq}
O(1)	0.05506(5)	−0.1784(3)	0.06829(9)	4.99(3)
O(2)	0.04632(4)	0.2087(3)	−0.04806(7)	4.75(3)
O(3)	0.10087(5)	−0.0139(3)	0.23677(8)	5.89(4)
C(1)	0.07017(6)	0.0925(4)	0.0910(1)	4.12(4)
C(2)	0.08871(6)	0.2159(4)	0.0339(1)	3.97(4)
C(3)	0.13617(6)	0.0735(4)	0.0399(1)	4.11(4)
C(4)	0.18023(6)	0.0840(4)	0.1283(1)	4.06(4)
C(5)	0.16179(7)	−0.0324(5)	0.1868(1)	4.44(5)
C(6)	0.11401(7)	0.1066(4)	0.1788(1)	4.33(4)
C(7)	0.22941(7)	−0.0525(5)	0.1384(1)	4.67(5)
C(8)	0.25327(8)	0.0669(6)	0.0887(2)	5.48(6)
C(9)	0.30576(10)	−0.0456(9)	0.1095(2)	7.10(8)
C(10)	0.04989(9)	0.4084(6)	−0.1002(1)	5.85(6)
C(11)	0.0646(1)	0.1343(8)	0.2506(2)	7.12(9)

the CH_2 hydrogen H(4) (the torsion angles H(4)-C(3)-C(4)-H(6) and H(3)-C(2)-C(3)-H(4) are 176° and −179°, respectively). The bond lengths and angles are in the usual ranges.

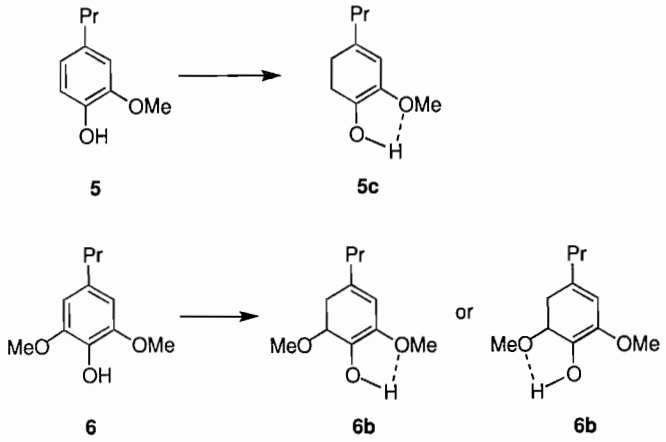
The ^{1}H NMR data of **6a** were then used to establish the relative stereochemistries of **5a** and **5b**. The equatorial methine proton in **6a** has an ^{1}H NMR signal at δ 4.31 while the two axial methine protons adjacent to the OMe groups have signals (m) centered at δ 3.13 (Fig. 3). Based on these assignments for **6a**, the major diastereomer **5a** is thus drawn as shown in Fig. 3, with its assigned ^{1}H NMR signals; the slightly lower δ 4.09 value for the equatorial proton in **5a** compared to that of **6a** (δ 4.31) is due to the presence of only one OMe group β to the proton. A similar effect is also seen in **4b** where there is no OMe group and the equatorial methine proton adjacent to the OH group is seen at δ ~3.94. The minor diastereomer **5b** has two one-proton signals at δ 3.45–3.57 and at δ 3.49–3.56. This is possible only when the methine protons adjacent to the OH and the OMe groups are in the axial and equatorial position, respectively (Fig. 3).

The formation of a predominant or an exclusive *cis* diastereomer must be due to a "continuous" substrate coordination mechanism involved in the hydrogenation, similar to the situation found by others using Co(I)–phosphite complexes for the catalytic hydrogenation of arenes (18) (i.e., the arene substrate remains coordinated throughout successive hydrogen transfer from the metal to give addition of hydrogen on one side of the substrate via η^6-, η^4-, η^3-, and η^2-hydrocarbon moieties). The formation of a small amount of *trans* diastereomer in the hydrogenation of **4** and **5** likely arises from the enol–keto tautomerization of the hydrogenation intermediates. Hydrogenation of the first C=C double bond of the aromatic ring of **4** at the less sterically hindered position will give enol **4d**, which can either hydrogenate directly to the *cis* diastereomer **4b** via the "continuous" substrate coordination mechanism or tautomerize to **4e** and then hydrogenate to **4b** and **4c** through **4a** (Scheme 2). The isolation of **4a** and its further hydrogenation to **4b** and **4c** are consistent with such an enol–keto tautomerization.

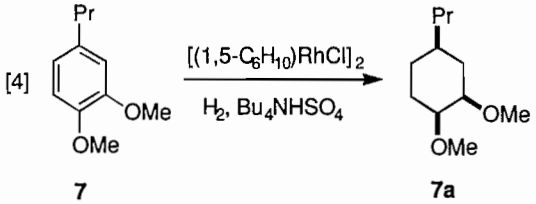
Hydrogenation of the first C=C double bond of the aromatic ring of **5** at the least sterically hindered position will give enol **5c**, which is likely stabilized by the OMe substituent via the formation of an intramolecular H-bond (Scheme 3). The opportunities for H-bonding are increased and, hence, the enol is more likely stabilized when a second OMe substituent is present adjacent to the OH group, as in the hydrogenation of **6** (Scheme 3). This increasing enol stabilization could account for the increasing *cis* diastereoselectivity for the hydrogenation of substrates **4**, **5**, and **6**, respectively.

Additional evidence for the contribution of such an enol–keto tautomerization to the formation of the *trans* diastereomer was obtained when we carried out the hydrogenation of 1,2-dimethoxy-4-propylbenzene (**7**). Only *cis,cis*-1,2-dimethoxy-*cis*-4-propylcyclohexane (**7a**) was isolated (eq. [4]). The relative stereochemistry of **7a** was established in a way similar to that used to define the stereochemistries of **5a**

Scheme 3. Stabilization of enols **5c** and **6b** via the formation of intramolecular H-bonds.



and **5b**. The stereoselective hydrogenation of a similar but simpler compound, *p*-methylanisole, to *cis*-4-methylcyclohexyl methyl ether has been reported by others (14).



The active Rh catalyst is probably present in a colloidal form: as the hydrogenation proceeds, metal particles accumulate and these are not active for subsequent hydrogenation reactions. The presence of the aqueous buffer and Bu_4NHSO_4 (a phase-transfer reagent) (14) is essential for effective catalysis.

Experimental section

General procedures

All the hydrogenation reactions were monitored by TLC and (or) GC. Analytical TLC was performed on aluminum-backed, precoated silica gel plates (E. Merck, type 5554), which were "visualized" by UV fluorescence or by heating after spraying with a mixture of MeOH, HOAc, H_2SO_4, and anisaldehyde (90:10:5:1 by volume). GC analysis was carried out on a Hewlett Packard model 5890 GC with an FID detector and a Carbowax column. Flash column chromatography (19) was performed using Silica Gel 60, 230–400 mesh ASTM (E. Merck). Infrared spectra were recorded on a Bomem Michelson 100 FT-IR spectrophotometer using internal calibration; liquid samples were placed between two 3-mm NaCl plates, and solid samples were dissolved in $CHCl_3$. ^1H NMR spectra were recorded on Bruker WH-400 or Varian XL-300 spectrometers; chemical shifts (δ) were measured in $CDCl_3$ using TMS as the internal standard. LRMS and HRMS spectra were determined on a Kratos-AEI model MS 50 spectrometer operating at 70 eV.

Materials

Propylphenol (**4**) was obtained from Aldrich and purified by vacuum distillation (20). 2-Methoxy-4-propylphenol (**5**), 2,6-dimethoxy-4-propylphenol (**6**), and 1,2-dimethoxy-4-propylbenzene (**7**) were prepared as described below. $RhCl_3 \cdot 3H_2O$ was obtained from Johnson Matthey Ltd; $[(1,5\text{-}C_6H_{10})RhCl]_2$ was prepared by treatment of $RhCl_3 \cdot 3H_2O$ with 1,5-hexadiene in aqueous EtOH according to the literature (21). All other reagents and solvents were obtained from Aldrich and used without further purification.

Preparation of 2-methoxy-4-propylphenol (5) (ref. 22)

To 2.07 g (12.6 mmol) of eugenol (4-allyl-2-methoxyphenol) in 40 mL of EtOH was added 268 mg of 5% Pd on charcoal (0.126 mmol in Pd). The solution was deaerated using the freeze–pump–thaw technique. H_2 at 1 atm was bubbled through the stirred solution overnight at room temperature. The Pd catalyst was filtered off and EtOH was removed under reduced pressure. Et_2O (40 mL) was introduced to the residue and the solution was washed with saturated NaCl (2 × 20 mL), and dried over $MgSO_4$ for 30 min. Removal of the drying agent by filtration and removal of the solvent under reduced pressure gave the crude products, which were then purified by vacuum distillation to give 2.08 g (94%) of 2-methoxy-4-propylphenol (**5**): IR ν_{max}: 3476, 2958, 2930, 2867, 1608, 1514, 1459, 1430, 1367, 1268, 1234, 1151, 1123, 1034, 931, 846, 816, 795, 777, 736; ^1H NMR (300 MHz) δ: 0.93 (t, 3H), 1.53–1.70 (m, 2H), 2.51 (t, 2H), 3.89 (s, 3H), 5.44 (s, 1H), 6.63–6.89 (m, 3H); mass spectrum (EI), *m/z*: 166 (M^+: 30.7); HRMS calcd.: 166.0994; found: 166.0994.

Preparation of 2,6-dimethoxy-4-propylphenol (6)

The procedure was as described for **5**. 4-Allyl-2,6-dimethoxyphenol (9.50 g, 48.9 mmol) was hydrogenated with 1.03 g of 5% Pd/C in 100 mL of EtOH to give 8.53 g (89%) of **6**: IR ν_{max}: 3477, 2944, 2869, 2841, 1610, 1514, 1458, 1427, 1344, 1321, 1279, 1239, 1214, 1150, 1111, 1035, 967, 915, 824, 801, 770, 738; ^1H NMR (300 MHz) δ: 0.94 (t, 3H), 1.56–1.70 (m, 2H), 2.51 (t, 2H), 3.88 (s, 6H), 5.37 (s, 1H), 6.40 (s, 2H); mass spectrum (EI), *m/z*: 196 (M^+: 30.1); HRMS calcd.: 196.1099; found: 196.1096.

Preparation of 1,2-dimethoxy-4-propylbenzene (7)

The procedure was as described for **5**. 4-Allyl-1,2-dimethoxybenzene (8.99 g, 50.5 mmol) was hydrogenated with 1.07 g of 5% Pd/C in 100 mL of EtOH to give 9.01 g (99%) of **7**: IR ν_{max}: 2996, 2956, 2932, 2868, 2834, 1606, 1589, 1513, 1458, 1415, 1377, 1333, 1262, 1236, 1188, 1156, 1140, 1030, 938, 846, 806, 762; ^1H NMR (300 MHz) δ: 0.93 (t, 3H), 1.58–1.69 (m, 2H), 2.53 (t, 2H), 3.88 (s, 3H), 3.89 (s, 3H), 6.68–6.87 (m, 3H); mass spectrum (EI), *m/z*: 180 (M^+: 24.7); HRMS calcd.: 180.1150; found: 180.1145.

Catalytic hydrogenation of 4-propylphenol (4) (ref. 14)

To 28 mg (0.063 mmol) of $[(1,5\text{-}C_6H_{10})RhCl]_2$ in 10 mL of hexane were added **4** (857 mg, 6.30 mmol) dissolved in 5 mL of hexane, Bu_4NHSO_4 (135 mg, 0.40 mmol), and 5 mL of an aqueous buffer of pH 7.5 (boric acid, citric acid, and sodium phosphate) (23). The solution was deaerated using the freeze–pump–thaw technique. H_2 was then bubbled through the stirred solution at room temperature under atmospheric pressure. Upon the completion of the reaction (~50 h), the metal particles that accumulated as the reaction proceeded were removed by suction filtration. The filtrate was diluted with

25 mL of Et_2O. The organic layer was separated, washed twice with saturated NaCl (2 × 20 mL), and dried over $MgSO_4$ for 30 min. Removal of the drying agent by filtration and removal of the solvent under reduced pressure gave the crude products, which were then separated by flash column chromatography (silica gel) using a mixture of hexanes and ethyl acetate (9:1 by volume) as the eluent to give 88 mg (10%) of 4-propylcyclohexanone (**4a**): IR ν_{max}: 2940, 2865, 1716, 1454, 1377, 1329, 1241, 1172, 1123, 1071, 943, 882, 816, 743; ^{1}H NMR (300 MHz) δ: 0.72–1.02 (m, 3H), 1.15–1.52 (m, 5H), 1.53–1.80 (m, 2H), 1.96–2.12 (m, 2H), 2.25–2.42 (m, 4H); mass spectrum (EI), *m/z*: 140 (M^+: 38.3); HRMS calcd.: 140.1201; found: 140.1197; 528 mg (59%) of *cis*-4-propylcyclohexanol (**4b**): IR ν_{max}: 3360, 2931, 2864, 1453, 1371, 1334, 1253, 1209, 1141, 1064, 1049, 1033, 1021, 961, 927, 908, 885, 865, 819, 734; ^{1}H NMR (400 MHz) δ: 0.87 (t, 3H), 1.14–1.42 (m, 7H), 1.43–1.62 (m, 5H), 1.63–1.72 (m, 2H), 3.90–3.98 (m, 1H); mass spectrum (EI), *m/z*: 142 (M^+: 2.7); HRMS calcd.: 142.1358; found: 142.1350; and 179 mg (20%) of *trans*-4-propylcyclohexanol (**4c**): IR ν_{max}: 3343, 2933, 2860, 1456, 1370, 1246, 1204, 1146, 1096, 1054, 1010, 951, 906, 836, 734; ^{1}H NMR (400 MHz) δ: 0.86 (t, 3H), 1.10–1.33 (m, 9H), 1.47 (s, br, 1H), 1.70–1.78 (m, 2H), 1.90–2.00 (m, 2H), 3.48–3.57 (m, 1H); mass spectrum (EI), *m/z*: 142 (M^+: 0.5); HRMS calcd.: 142.1358; found: 142.1366.

Catalytic hydrogenation of 2-methoxy-4-propylphenol (5)

The hydrogenation procedure was as described for **4**. **5** (1.046 g, 6.30 mmol) was hydrogenated to give 748 mg (69%) of *cis*-2-methoxy-*cis*-4-propylcyclohexanol (**5a**): IR ν_{max}: 3468, 2933, 2867, 1459, 1440, 1378, 1328, 1267, 1225, 1194, 1158, 1137, 1110, 1089, 1020, 981, 942, 884, 868, 824, 784, 739; ^{1}H NMR (400 MHz) δ: 0.88 (t, 3H), 1.18–1.45 (m, 9H), 1.70–1.80 (m, 1H), 1.85 (s, br, 1H), 1.94–2.12 (m, 1H), 3.11–3.19 (m, 1H), 3.39 (s, 3H), 4.09 (m, 1H); mass spectrum (EI), *m/z*: 172 (M^+: 13.6); HRMS calcd.: 172.1464; found: 172.1464; and 119 mg (11%) of *cis*-2-methoxy-*trans*-4-propylcyclohexanol (**5b**): IR ν_{max}: 3425, 2956, 2928, 2870, 1459, 1374, 1260, 1211, 1180, 1097, 1058, 969, 806; ^{1}H NMR (400 MHz) δ: 0.89 (t, 3H), 1.12–1.38 (m, 6H), 1.42–1.62 (m, 2H), 1.68–1.77 (m, 2H), 1.80 (s, br, 1H), 2.02–2.12 (m, 1H), 3.38 (s, 3H), 3.45–3.57 (m, 1H), 3.49–3.56 (m, 1H); mass spectrum (EI), *m/z*: 172 (M^+: 8.0); HRMS calcd.: 172.1464; found: 172.1459.

Catalytic hydrogenation of 2,6-dimethoxy-4-propylphenol (6)

To 28 mg (0.063 mmol) of $[(1,5\text{-}C_6H_{10})RhCl]_2$ in 10 mL of hexane in a 25-mL glass liner were added **6** (1.235 g, 6.30 mmol) dissolved in 5 mL of hexane, Bu_4NHSO_4 (135 mg, 0.40 mmol), and 5 mL of the aqueous, pH 7.5 buffer. The solution was deaerated. The glass liner was inserted into a 60-mL laboratory stainless steel autoclave that had been flushed with N_2. The autoclave was sealed and pressurized with H_2 to 200 psi, and the reaction was allowed to proceed at room temperature under magnetic stirring. After 6 h, excess H_2 was carefully released. The metal particles were removed by suction filtration, and the filtrate was diluted with 25 mL of Et_2O. The organic layer was separated, washed twice with saturated NaCl (2 × 20 mL), and dried over $MgSO_4$ for 30 min. Removal of the drying agent by filtration and removal of the solvent under reduced pressure gave the crude product, which was purified by flash column chromatography (silica gel) using a mixture of hexanes and ethyl acetate (12:1 by volume) as the eluent and by recrystallization from EtOH to give 1.044 g (82%) of *cis,cis*-2,6-dimethoxy-4-cis-propylcyclohexanol (**6a**) as colorless crystals: IR ν_{max}: 3580, 3472, 2990, 2933, 2860, 2827, 1459, 1379, 1300, 1099, 994, 956, 900, 861; ^{1}H NMR (400 MHz) δ: 0.90 (t, 3H), 1.25–1.40 (m, 6H), 1.70–1.78 (m, 4H), 3.09–3.17 (m, 2H), 3.40 (s, 6H), 4.31 (s, br, 1H); mass spectrum (EI), *m/z*: 202 (M^+: 0.3); HRMS calcd.: 202.1569; found: 202.1560.

X-ray crystallographic analysis of 6a

A colorless plate crystal of **6a** having approximately dimensions of 0.15 × 0.30 × 0.35 mm was mounted in a glass capillary. Unit-cell parameters were refined by least-squares on 2 sin θ/λ values for 25 reflections (75.10° < 2θ < 91.09°) measured on a Rigaku AFC6S diffractometer with graphite monochromated Cu-Kα radiation (λ(CuKα) = 1.54178 Å). Crystal data at 21°C are: $C_{11}H_{22}O_3$; FW = 202.29; a = 29.277(1) Å; b = 4.982(1) Å; c = 18.403(1) Å; β = 117.776(4)°; V = 2375.0(4) Å^3; Z = 8, ρ_{calc} = 1.131 g/cm^3; $F(000)$ = 896; μ (MoKα) = 6.47 cm^{-1}. Absent reflection: hkl ($h + k \neq 2n$), $h0l$ ($l \neq 2n$), space group = $C2/c$ (no. 15).

The data were collected at a temperature of 21 ± 1°C using the ω–2θ scan technique to a maximum 2θ value of 155.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.25° with a take-off angle of 6.0°. Scans of (1.00 + 0.20 tan θ)° were made at a speed of 16.0°/min (in ω). The weak reflections (I < 40.0σ(I)) were rescanned (maximum of 8 rescans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 285 mm. Of the 2781 reflections that were collected, 2725 were unique (R_{int} = 0.028); equivalent reflections were merged. The intensities of three representative reflections were measured after every 200 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Cu-Kα radiation is 6.5 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.73 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 9.1(3) × 10^{-6}).

The structure was solved by direct methods (24) and expanded using Fourier techniques (25). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement was based on 1537 observed reflections (I > 3.00 σ(I)) and 216 variable parameters and converged (largest parameter shift was 0.005 times its esd) with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.036$, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.041$. The standard deviation of an observation of unit weight was 2.55. The weighting scheme was based on counting statistics. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the

final difference Fourier map corresponded to 0.13 and −0.11 e/Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber (26). Anomalous dispersion effects were included in F_{calc} (27); the values for $\Delta f'$ and $\Delta f''$ and the mass attenuation coefficients were taken from the literature (28, 29). All calculations were performed using the *teXsan* crystallographic software package of Molecular Structure Co.[2] A listing of bond lengths, bond angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, and intermolecular contacts are included as supplementary materials (Tables S1–S6).[3] Measured and calculated structure factor amplitudes are available from the authors.

Catalytic hydrogenation of 1,2-dimethoxy-4-propylbenzene (7)

The hydrogenation procedure was as given for **4**. **7** (1.135 g, 6.30 mmol) was hydrogenated to give 927 mg (79%) of *cis,cis,cis*-1,2-dimethoxy-4-propylcyclohexane (**7a**): IR ν_{max}: 2930, 2871, 2825, 1456, 1377, 1307, 1192, 1163, 1114, 1096, 983, 946, 851, 786, 739; ^{1}H NMR (400 MHz) δ: 0.89 (t, 3H), 1.11–1.44 (m, 9H), 1.72–1.81 (m, 1H), 2.01–2.10 (m, 1H), 3.10–3.18 (m, 1H), 3.37 (s, br, 6H), 3.63 (s, br, 1H); mass spectrum (EI), *m/z*: 186 (M^+: 9.7); HRMS calcd.: 186.1620; found: 186.1614.

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[2] TEXSAN/TEXRAY structure analysis package (Version 5.1), Molecular Structure Corp., The Woodlands, Tex. 1985.

[3] Supplementary materials mentioned in the text may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. The tables of bond lengths, bond angles, and hydrogen atom parameters have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.