bubbler and covered with aluminum foil were added 40 mL of dry benzene and *t*-BuMgCl (2M, 10 mL, 20 mmol) in Et_2O. The reaction mixture was heated for 1 h at 50 °C to give a clear yellow solution. When the flask is not covered with aluminum foil, a brown mixture usually results. To the solution obtained previously was added 1-octyne (2.24 g, 20 mmol). The resulting mixture was heated for 6 h at 50 °C. Analysis of a small aliquot by ^1H NMR spectroscopy indicated that a singlet at δ 5.79 for the Cp group of *i*-BuZrCp$_2$Cl had cleanly shifted to δ 5.89 and that (*E*)-(1-octenyl)zirconocene chloride had been formed in 95% yield along with a nearly 100% yield of isobutylene (a multiplet at δ 4.75). After removal of the volatiles, the NMR spectra of (*E*)-(1-octenyl)zirconocene chloride were recorded with use of C_6D_6 as a solvent: ^1H NMR (C_6D_6, Me_4Si) δ 0.91 (t, *J* = 7 Hz, 3 H), 1.2–1.6 (m, 8 H), 2.11 (q, *J* = 7 Hz, 2 H), 5.89 (s, 10 H), 6.87 (dt, *J* = 18 and 2 Hz, 1 H), (the signal for the α-alkenyl proton was not discernible); ^{13}C NMR (C_6D_6, Me_4Si) δ 14.40, 23.18, 29.59, 29.75, 32.31, 38.89, 113.15, 143.13, 176.38. These spectra indicated an isomeric purity of ≥98%. Analysis of a protonated aliquot by GLC also indicated the formation of 1-octene in 91% yield without the contamination by *n*-octane.

Another 5-mmol aliquot was evaporated, dissolved in 10 mL of Et_2O, and treated with D_2O at 0 °C. The resultant mixture was sequentially treated with 3 N HCl, extracted with Et_2O, washed with aqueous $NaHCO_3$, and dried over $MgSO_4$. Distillation gave 395 mg (70% yield) of (*E*)-1-deuterio-1-octene:[7] bp 112–114 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.88 (t, *J* = 6 Hz, 3 H), 1.2–1.5 (m, 8 H), 2.04 (q, *J* = 7 Hz, 2 H), 4.98 (d, *J* = 17 Hz, 1 H), 5.81 (dt, *J* = 17 and 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.11, 22.66, 28.86, 28.95, 31.77, 33.80, 113.82 (t, *J* = 24 Hz), 139.15.

Hydrozirconation–Protonolysis of Alkynes. The following alkynes were converted to the corresponding alkenes following the representative procedure. **(a) 1-(Trimethylsilyl)-1-octyne.** The title compound (0.36 g, 2.0 mmol) was converted to 0.28 g (75%, 93% by GLC) of (*Z*)-1-(trimethylsilyl)-1-octene.[8] **(b) 4-(Pentynylthio)benzene.** The title compound (0.19 g, 1.0 mmol) gave 0.14 g (80%, 90% by GLC) of 4-(pentenylthio)-benzene.[9] **(c) 2-(3-Butynoxy)tetrahydro-2*H*-pyran.** The title compound (0.15 g, 1.0 mmol) was converted to 0.12 g (77%, 80% by GLC) of 2-(3-butenoxy)tetrahydro-2*H*-pyran.[10]

Hydrozirconation–Iodinolysis of Alkynes. (a) 1-Hexyne. Representative Procedure. 1-Hexyne (0.17 g, 0.23 mL, 2.0 mmol) was hydrozirconated as described earlier. The reaction mixture was cooled to −30 °C, treated with iodine (0.76 g, 3 mmol) in 3 mL of THF, warmed to 25 °C, and quenched with 3 N HCl. Analysis by GLC indicated the formation of (*E*)-1-iodo-1-hexene in 90% yield. The mixture was extracted with pentane, washed with aqueous $Na_2S_2O_3$, $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated. Filtration through a silica gel pad (pentane) followed by evaporation afforded 0.35 g (84%) of (*E*)-1-iodo-1-hexene:[11] ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, *J* = 7 Hz, 3 H), 1.2–1.5 (m, 4 H), 2.0–2.1 (m, 2 H), 5.97 (dt, *J* = 15 and 1.5 Hz, 1 H), 6.50 (dt, *J* = 15 and 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4) δ 13.98, 22.18, 30.70, 35.97, 74.63, 147.31. **(b) Phenylethyne.** The title compound (0.18 g, 1.8 mmol) was hydrozirconated in 90–92% yield. Iodinolysis with 0.63 g (2.5 mmol) of I_2 in 3 mL of THF afforded 0.28 (68%) of (*E*)-β-iodostyrene.[11] **(c) 4-Octyne.** The title compound (0.33 g, 3.0 mmol) was converted to 0.57 g (80%) of (*E*)-4-iodo-4-octene.[12] **(d) 5-Chloro-1-pentyne.** The title compound (0.10 g, 1 mmol) was converted to 0.16 g (68%) of (*E*)-5-chloro-1-iodo-1-pentene.[13] **(e) 3-(*tert*-Butyldimethylsiloxy)-1-octyne.** The title compound (0.72 g, 3.0 mmol) was converted to 0.88 g (80%) of (*E*)-3-(*tert*-butyldimethylsiloxy)-1-iodo-1-octene.[14]

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Supplementary Material Available: Experimental data for products formed (1 page). Ordering information is given on any current masthead page.

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Two New Abnormal Pathways in the Para-Claisen Rearrangement of 2-(Allyloxy)- and 2-(Crotyloxy)-3-hydroxybenzaldehyde†

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As part of another project, we needed access to fairly large quantities of 5-allyl-2,3-dihydroxybenzaldehyde (**2a**). The obvious route to **2a** would involve the para-Claisen rearrangement[1] of the known compound 2-(allyloxy)-3-hydroxybenzaldehyde (**1a**). Compound **1a** was prepared as described[2,3] by regioselective alkylation of the monoanion of 2,3-dihydroxybenzaldehyde and thermolyzed neat at 160–170 °C. Unexpectedly, four products were obtained (Scheme I).

The major product, obtained in 50% yield, was indeed the desired 4-allyl isomer **2a**, accompanied by the expected decarbonylation product **5a**, and two other new compounds **3a** and **4a**. Insight into the nature of these rearrangements was obtained by repetition of the sequence with the crotyl analogue **1b**, which shows unequivocally that the reactions proceed exclusively by intramolecular concerted [3,3]-rearrangements.[4] There was no sign of allylic scrambling, which would be indicative of a fragmentation–recombination mechanism. The structures of **3a** and **4a** were confirmed by unambiguous synthesis (Scheme II). Thus, alkylation of the dianions of 3,4- and 2,3-dihydroxybenzaldehyde with allyl bromide takes place regiospecifically at the more basic meta phenoxide oxygen,[3] affording **6** and **7**, respectively. On thermolysis, an ordinary Claisen rearrangement to the vacant ortho position occurs, giving **3a** and **4a**. Interestingly, the temperature required to rearrange **6** was some 40 °C lower than that for isomer **7**.[5]

To the best of our knowledge, the meta-Claisen rearrangement of **1a,b** to **4a,b** is unprecedented. Neither can we find a precedent for the formation of **3a,b**.[6] These results are rationalized as shown in Scheme III.

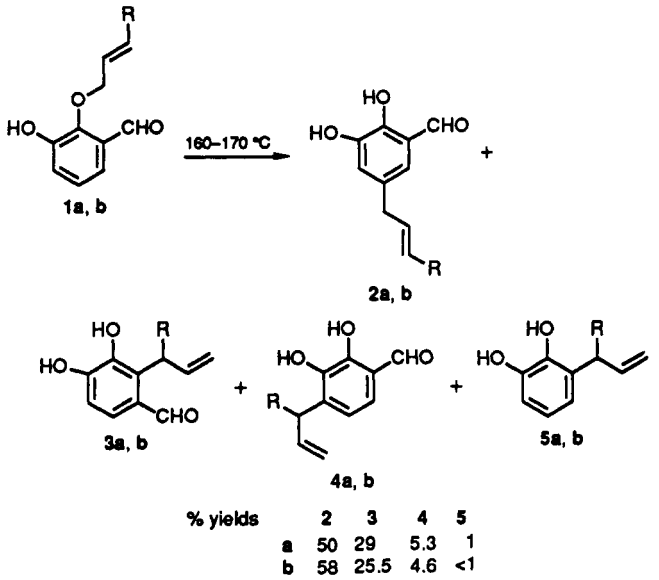
We assume that the first [3,3]-sigmatropic shift occurs on the aldehyde side. The resulting cyclohexadienone intermediate has three possibilities: loss of CO giving **5**, [1,2]-shift of the formyl group to give the abnormal product **3**, or another [3,3]-shift. In the latter case, enolization gives the major product **2**. Alternatively, the allyl or crotyl group can undergo a [2,3]-shift, affording **4**.

Since, in this rationalization, **4** is derived by rearrangement of an enolizable cyclohexadienone, it should be possible to influence the product ratio by altering the rate of enolization. Schmid et al.[7] have shown that the further

† For the sake of brevity "allyl" and "crotyl" are used throughout instead of "2-propenyl" and "(*E*)-2-butenyl".

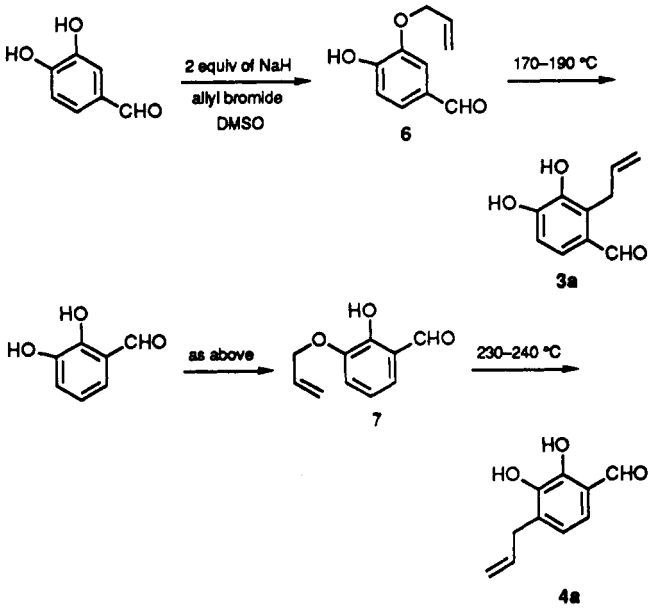
0022-3263/91/1956-2591$02.50/0

Scheme I



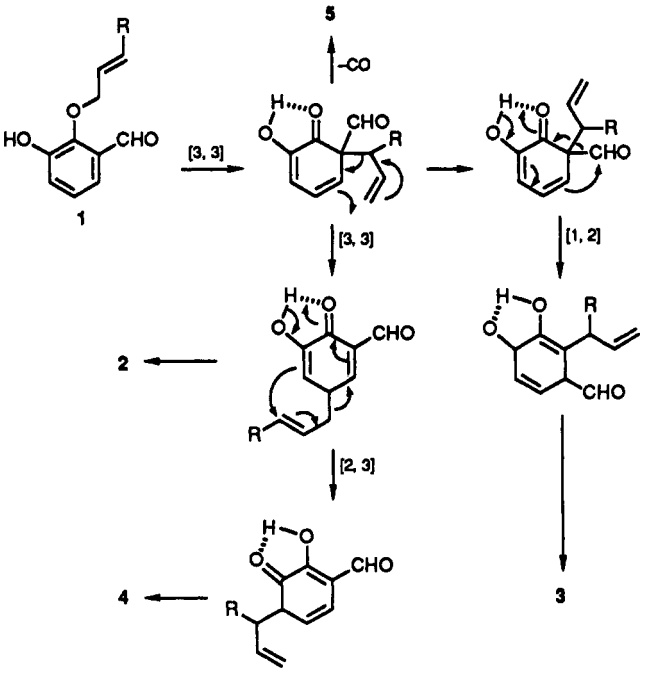
% yields	2	3	4	5
a	50	29	5.3	1
b	58	25.5	4.6	<1

Scheme II

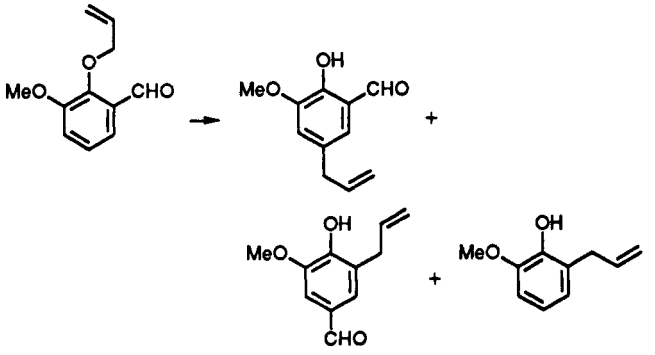


rearrangement of an *o*-cyclohexadienone to the para isomer can be effectively suppressed by changing the solvent of the Claisen rearrangement from decalin (in which enolization is slow) to DMF (in which it is fast). Indeed, when **1a** was thermolyzed in DMF, essentially only **2a**, **3a**, and **5a** were formed, with at most a trace of **4a**, whereas **4a** was produced abundantly when the rearrangement was performed in decalin.

Scheme III



Scheme IV



Other mechanistic possibilities for the formation of **4** which do not pass via an enolizable intermediate (e.g. a [3,5]-shift followed by a [2,3]-shift) are in all probability excluded by this solvent effect. Furthermore, a [3,5]-sigmatropic rearrangement would be allowed thermally only with a sterically unfavorable antarafacial stereochemistry with respect to one component. The proposed mechanism requires the presence of an intramolecular hydrogen bond to conduct the electron flow around the ring. The importance of this bond is shown by the totally different pathways followed in the Claisen rearrangement of 2-(allyloxy)-3-methoxybenzaldehyde[8] (Scheme IV). No trace of products corresponding to **3** and **4** was reported, a result we have confirmed.

Experimental Section

NMR spectra were recorded at 60 MHz with TMS as reference. Melting points are corrected. TLC was performed with Merck precoated silica 60 F plates (0.2 mm thickness) and spots were visualized with phosphomolybdic acid. Column chromatography

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(5) We ascribe this difference in activation energy to the fact that in **6** and **1a,b** the intermediate cyclohexadienone can be stabilized by a strong intramolecular hydrogen bond between the newly formed keto function and the adjacent hydroxy group. In **7** no stabilization accrues to the cyclohexadienone because the OH group is already hydrogen bonded to the aldehyde carbonyl.
(6) There are a few examples of [1,5]-migration of acetyl groups in the Claisen rearrangement. See: Bender, D. R.; Kanne, D.; Frazier, J. D.; Rapoport, H. *J. Org. Chem.* **1983**, *48*, 2709. Falshaw, C. P.; Lane, S. A.; Ollis, W. D. *J. Chem. Soc., Chem. Commun.* **1983**, 491. See also Scheme IV for a [1,3]-migration of a formyl group.
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was done using the flash method on Merck silica 60 (230–400-mesh ASTM). Solvents and reagents were used as received, with the exception of allyl bromide, which was freshly redistilled. Dimethyl sulfoxide (DMSO) (Merck Art 2931) was from freshly opened bottles.

3-Hydroxy-2-(2-propenyloxy)benzaldehyde (1a). This was prepared on a 0.1-mol scale in 62% yield by the alkylation of 2,3-dihydroxybenzaldehyde with 1 equiv of sodium hydride and allyl bromide in DMSO according to the method of van Staveren et al.[2,3] The chromatographic purification could be avoided by triturating the crude product several times with boiling hexane. On cooling the hexane extract, the title compound crystallized as shining plates, mp 80–81 °C (lit.[2] mp 80–81 °C). NMR and IR data were in accord with literature values.

(*E*)-2-(2-Butenyloxy)-3-hydroxybenzaldehyde (1b). Substitution of allyl bromide by crotyl bromide in the above procedure afforded the title compound in 58% yield as plates: mp 78–79 °C; IR (KBr) 3500–2500, 1650, 1610, 1590, 1500, 1370 cm^{-1}; NMR ($CDCl_3$) δ 1.70 (br d, 3 H, J = 4 Hz), 4.45 (m, 2 H), 5.70 (m, 2 H), 6–6.5 (br, 1 H, D_2O exch), 6.95–7.40 (m, 3 H), 10.15 (s, 1 H). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.90; H, 6.34.

Thermal Rearrangement of 3-Hydroxy-2-(2-propenyloxy)benzaldehyde (1a). *Caution*! The reaction becomes vigorous and exothermic when heated above 200 °C, especially on a large scale. 3-Hydroxy-2-(2-propenyloxy)benzaldehyde (1a) (5.06 g, 28.43 mmol) was placed in a 25-mL round-bottomed flask equipped with a magnetic stirring bar and an air condenser. The flask was gently heated to melt the solid and then placed in a Wood's metal bath at 165–170 °C. After an induction period of a few minutes the liquid in the flask darkened and evolved a gas. TLC analysis of the resulting black mixture (65:35:1 hexane/ethyl acetate/acetic acid) showed four spots at R_f 0.6 (**4a**), 0.5 (**2a**), 0.35 (**5a**), and 0.17 (**3a**). After cooling, the mixture was triturated 10 times with boiling hexane. The dark, granular residue, consisting largely of **3a**, was dissolved in ethyl acetate and adsorbed on 10 g of silica, which was then applied to the top of a silica column. Elution with 65:35:1 hexane/ethyl acetate/acetic acid afforded **3,4-dihydroxy-2-(2-propenyl)benzaldehyde (3a)** (1.45 g, 29%) as a crystalline solid with a faint mauve tinge, mp 133–138 °C. Recrystallization from hexane/ethyl acetate raised the melting point to 137–138.5 °C: IR (KBr) 3500, 3100, 2980, 1660, 1620, 1590, 1510 cm^{-1}; NMR ($CDCl_3$ + DMSO-d_6) δ 3.80 (br d, 2 H, J = 7 Hz), 4.80 (m, 1 H), 5.05 (m, 1 H), 6.03 (m, 1 H), 6.75 (d, 1 H, J = 9 Hz), 7.2 (d, 1 H, J = 9 Hz), 7.5–8.5 (br, 2 H, D_2O exch), 9.85 (s, 1 H). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.65. Found: C, 67.22; H, 5.59.

The hexane extracts were evaporated and chromatographed on silica with 80:20:1 hexane/ethyl acetate/acetic acid as eluant. First to elute was **2,3-dihydroxy-4-(2-propenyl)benzaldehyde (4a)** (270 mg, 5.3%), followed by **2,3-dihydroxy-5-(2-propenyl)benzaldehyde (2a)** (2.53 g, 50%), both pale yellow crystalline solids. The last compound to appear was **1,2-dihydroxy-3-(2-propenyl)benzene (5a)** (49 mg, 1%) as an oil.

For **4a**: mp 50–51 °C; IR (KBr) 3480, 3400, 3080, 1650, 1575, 1510, cm^{-1}; NMR ($CDCl_3$) δ 3.40 (br d, 2 H, J = 7 Hz), 4.95 (m, 1 H), 5.15 (m, 1 H), 5.90 (m, 1 H), 6.70 (d, 1 H, J = 7 Hz), 6.95 (d, 1 H, J = 7 Hz), 9.70 (s, 1 H), 10.5 (br, 2 H, D_2O exch). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.65. Found: C, 67.71; H, 5.70.

For **2a**: mp 35–36 °C; IR (KBr) 3600, 3100, 2800, 3000, 2900, 1660 cm^{-1}; NMR ($CDCl_3$) δ 3.25 (br d, 2 H, J = 7 Hz), 4.85 (m, 1 H), 5.15 (m, 1 H), 6.0 (m, 1 H), 6.83 (br d, 1 H, J = 1 Hz), 6.90 (br d, 1 H, J = 1 Hz), 9.65 (s, 1 H), 10.5–11 (br, 2 H, D_2O exch). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.65. Found: C, 67.29; H, 5.71.

For **5a**: IR no carbonyl; NMR ($CDCl_3$) δ 3.35 (br d, 2 H, J = 7 Hz), 4.95 (m, 1 H), 5.20 (m, 1 H), 5.80 (m, 1 H), 5–6 (br, 2 H, D_2O exch), 6.65 (br s, 3 H).

Rearrangement of 1a in DMF and Decalin. A sample of **1a** (ca. 10 mg) was dissolved in DMF (2 mL) and heated in a sealed tube at 170–175 °C for 1 h. The reaction mixture was partitioned beween water and ethyl acetate. TLC analysis (65:35:1 hexane/ethyl acetate/acetic acid) of the organic phase showed two strong spots at R_f 0.5 (**2a**) and 0.17 (**3a**) and a weak one at 0.35 (**5a**), but no appreciable trace of **4a** at R_f 0.6. A control experiment indicated that the absence of **4a** was not due to its instability under the reaction conditions. The procedure was repeated with decalin (2 mL) replacing DMF. The reaction mixture was diluted with toluene, and the phenolic material was extracted twice with 1 M NaOH solution. The alkaline layer was acidified and extracted with ethyl acetate, TLC analysis of which showed the clear and unequivocal presence of **4a** as well as the other three products.

Thermal Rearrangement of (*E*)-2-(2-Butenyloxy)-3-hydroxybenzaldehyde (1b). A sample of **1b** (3.84 g, 20.0 mmol) was subjected to the conditions used for the rearrangement of **1a**. TLC analysis of the resulting dark mixture (65:35:1 hexane/ethyl acetate/acetic acid) showed four spots at R_f 0.60 (**4b**), 0.55 (**2b**), 0.40 and 0.15 (**3b**). The mixture was chromatographed on silica with 80:20:1 hexane/ethyl acetate/acetic acid to give, after rechromatography of the mixed fractions, 176 mg (4.6%) of **2,3-dihydroxy-4-(3-(1-butenyl))benzaldehyde (4b)**, 2.21 g (58%) of **(*E*)-5-(1-(2-butenyl))-2,3-dihydroxybenzaldehyde (2b)**, 51 mg of a mixture possibly containing **5b**, and 980 mg (25.5%) of **2-(3-(1-butenyl))-3,4-dihydroxybenzaldehyde (3b)**, all as oils. On standing, **2b** crystallized to plates. The third, minor fraction on closer examination proved to be a complex mixture and was not examined further.

For **4b**: IR (KBr) 3500–3000, 1650, 1575, 1510 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (3 H, d, J = 9 Hz), 3.95 (br quintet, 1 H, J = 9 Hz), 4.90 (m, 1 H), 5.15 (m, 1 H), 5.5–6.0 (br, 1 H, D_2O exch), 6.03 (m, 1 H), 6.70 (d, 1 H, J = 8 Hz), 6.97 (d, 1 H, J = 8 Hz), 9.68 (s, 1 H), 11–12 (br, 1 H, D_2O exch). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.48; H, 6.24.

For **2b**: mp 51–52 °C; IR (KBr) 3500–3000, 2940, 2870, 1660, 1610 cm^{-1}; NMR ($CDCl_3$) δ 1.66 (br s, 3 H), 3.20 (br s, 2 H), 5.45 (m, 2 H), 6.86 (br s, 1 H), 6.90 (br s, 1 H), 7.0–8.5 (br, 2 H, D_2O exch), 9.68 (s, 1 H). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.44; H, 6.21.

For **3b**: IR (KBr) 3500–3000, 1665, 1600, 1580 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (d, 3 H, J = 9 Hz), 4.85 (m, 1 H), 5.05 (m, 1 H), 5.25 (m, 1 H), 6.20 (m, 1 H), 6.80 (d, 1 H, J = 8 Hz), 6.7–7.0 (br, 2 H, D_2O exch), 7.25 (d, 1 H, J = 8 Hz), 9.90 (s, 1 H). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.59; H, 6.33.

4-Hydroxy-3-(2-propenyloxy)benzaldehyde (6). Sodium hydride (3.80 g of 60% dispersion in mineral oil, 81 mmol) was washed free of oil with four portions of hexane under nitrogen. Dry DMSO (60 mL) was then added. With stirring and cooling, a solution of 3,4-dihydroxybenzaldehyde (5.51 g, 40 mmol) in DMSO (20 mL) was added dropwise. After 20 min a solution of allyl bromide (4.84 g, 40 mmol) in DMSO (20 mL) was added. The reaction mixture was stirred overnight at ambient temperature, poured into ice water, and acidified with dilute HCl. The product was extracted with ethyl acetate (3 × 100 mL), washed with brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica with 80:20:1 hexane/ethyl acetate/acetic acid as eluant to give 3.1 g (43%) of the title compound **6a** as a colorless solid, mp 60–61 °C (lit.[9] mp 58–61 °C). The NMR data matched those reported by Reitz et al.[9]

2-Hydroxy-3-(2-propenyloxy)benzaldehyde (7). Repetition of the above procedure with 2,3-dihydroxybenzaldehyde yielded 3.50 g (48%) of the title compound as a yellow oil after chromatography: IR (KBr) 3340, 3200, 1650, 1610, 1580 cm^{-1}; NMR ($CDCl_3$) δ 4.5 (br d, 2 H, J = 7 Hz), 5.15 (m, 1 H), 5.35 (br d, 1 H, J = 10 Hz), 6.05 (m, 1 H), 7.00 (m, 3 H), 9.70 (s, 1 H), 10–11 (br, 1 H, D_2O exch). Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.65. Found: C, 67.55; H, 5.70.

Rearrangement of 6 and 7. A sample of **6** (500 mg, 3.81 mmol) was heated for 3 min at 190–200 °C under an atmosphere of N_2. TLC analysis (73:30:1 hexane/ethyl acetate/acetic acid) showed the complete disappearance of the starting material at R_f 0.35 and its replacement by **3a** at R_f 0.14. The dark reaction mixture was taken up in ethyl acetate and adsorbed on 5 g of silica. Chromatography of this material with 65:35:1 hexane/ethyl acetate/acetic acid as eluant afforded 403 mg (80%) of **3a** which was identical with material prepared by thermolysis of **1a** by all the usual criteria (IR, NMR, TLC, mp, and mmp). Thermolysis of 750 mg (4.21 mmol) of **7** at 240–250 °C for 10 min under N_2, followed by isolation as above afforded 450 mg (60%) of **4a**, identical with material previously prepared from **1a**.

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A Study of the Catalytic Deuteration of 1,4-Butynediol

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The stereoselective semihydrogenation of alkynes is an important and useful reaction in organic chemistry.[1] Recently, the stereoselective hydrogenation of 1,4-butynediol to 1,4-butenediol using an interlamellar montmorillonite–diphenylphosphinepalladium(II) complex has been reported.[2] The reaction proceeds with high selectivity (97%), and no reduction of the alkene was observed with the absorption of 1 equiv of hydrogen.

We have been interested in catalytic reduction to stereospecifically introduce deuterium into butynediol[3] and related dialkyl maleates and fumarates.[4] Partial hydrogenation of 1,4-butynediol with a variety of partially poisoned catalysts has been reported.[5] Our previous work has involved the use of Lindlar catalyst, which we found to catalyze the uptake of deuterium very slowly. Large-scale reduction of 1,4-butynediol required weeks for completion, and the isolated yield of the olefin was reduced from overreduction if the reaction was not carefully monitored and from competing condensation or polymerization reactions.

We report the results of our studies relating to the reduction of 1,4-butynediol using Lindlar catalyst, 5% palladium on charcoal, and montmorillonite–diphenylphosphinepalladium(II) complex. This study was prompted by (1) a need for a convenient large-scale production of both *cis*-2,3-dideuteriobutenediol (200–500 g) and 2,2,3,3-tetradeuteriobutanediol[6] and (2) an interest in understanding why the use of 5% palladium on charcoal or Lindlar catalyst produces both low chemical and isotopic yields of the 1,4-butanediol-d_4 when the reduction is allowed to go to completion. We have previously reported the reduction of 1,4-butynediol to *cis*-2,3-dideuterio-2-butene-1,4-diol, an important precursor in the synthesis of chiral 2,3-dideuteriosuccinic acid.[3] We were particularly concerned about the possible implications that low deuterium incorporation in the two internal methylene groups of the saturated diol could have on the isotopic abundances in the vinyl positions of the corresponding butenediol precursor. The use of capillary gas chromatographic columns separated each of the reduced diols and significantly enhanced our ability to follow the course of the reductions.

The initial reduction of 1,4-butynediol with each of the catalysts mentioned previously proceeds smoothly, and the major product detected early in the reduction was *cis*-2,3-dideuterio-1,4-butenediol. The relative rates of reduction at 1 atm of pressure of deuterium gas at room temperature were as follows: montmorillonite–diphenylphosphinepalladium(II) complex > 5% palladium/carbon ≫ Lindlar catalyst. *cis*-2,3-Dideuterio-1,4-butenediol was isolated from these reductions in high yield provided the reaction was carefully monitored and terminated following the absorption of 1 equiv of reducing gas. The stereochemistry about the double bond was characterized by conversion of the cis diol to *dl*-2,3-dibromo-2,3-dideuteriobutane-1,4-diol,[7] isolated after purification in 52% yield. ^{1}H NMR analysis indicated high deuterium abundances at the vinyl positions, and ^{13}C NMR indicated the absence of detectable splittings due to deuterium at the methylene positions.

When the reduction was allowed to continue and all the butynediol was consumed, overreduction of the 1,4-butenediol was observed with all three catalysts. In addition to the formation of 1,4-butanediol, the reaction was complicated by competitive formation of a new peak with a much shorter gas chromatographic retention time. This new peak was formed by all three catalytic systems investigated and required the presence of hydrogen or deuterium gas. At low deuterium or hydrogen pressures (~1 atm or less), this product was produced in yields up to ~70% (Table I). *cis*-1,4-Butenediol allowed to stir in the presence of the catalyst under the reaction conditions in the absence of H_2 or D_2 was not affected. However, if hydrogen or deuterium gas was introduced, the new peak appeared along with the presence of the saturated 1,4-diol. This new material was found to be isomeric with *cis*-2-butene-1,4-diol by GCMS and was identified as 2-hydroxytetrahydrofuran by spectroscopic and chemical characterization. Formation of this material competes with reduction to 1,4-butanediol and is responsible for the low chemical and isotopic yield previously obtained in the recovered butane-1,4-diol. Under our reaction conditions, 2-hydroxytetrahydrofuran exists in equilibrium with 4-hydroxybutanal,[8] which complicated the initial spectral analysis. Our failure to detect this ether earlier was due in part to limitations of our analytical system and its volatility under the conditions used to vacuum distill 1,4-butanediol.

2-Hydroxytetrahydrofuran was identified by its spectral properties and by conversion to the known 2,4-dinitrophenylhydrazone derivative. The ^{13}C NMR chemical shifts of the small amount of 4-hydroxybutanal in equilibrium with the cyclic form were consistent with those previously reported for 4-hydroxybutanal prepared from 1,4-butanediol by bis(η^5-cyclopentadienyl)zirconium dihydride catalyzed Oppenauer oxidation.[9]

Table I summarizes the results obtained in this study. Reductions with the clay–Pd catalyst are fastest in THF,

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