JOC *Note*

Kishner's Reduction of 2-Furylhydrazone Gives 2-Methylene-2,3-dihydrofuran, a Highly Reactive Ene in the Ene Reaction

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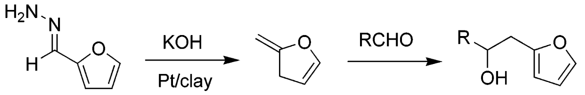
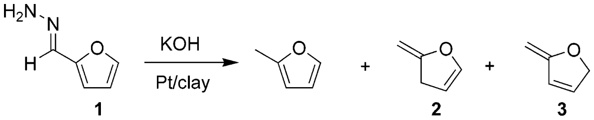


The Kishner reduction of 2-furylhydrazone gives 2-methylene-2,3-dihydrofuran as the major abnormal reduction product. 2-Methylene-2,3-dihydrofuran is an excellent ene in the carbonyl-ene reaction, reacting with a variety of aldehydes. Most notable was the asymmetric carbonyl-ene reaction of 2-methylene-2,3-dihydrofuran and decanal using $Ti(OCH(CH_3)_2)_4$/(*S*)-BINOL to give the corresponding alcohol in 66% yield and 94% ee. The reaction of 2-methylene-2,3-dihydrofuran with 2 equiv of 1,4-benzoquinone unexpectedly gave a monoalkylated 1,4-hydroquinone/1,4-benzoquinone electron donor−acceptor complex.

Kishner and Wolff independently developed the reduction of aldehydes and ketones to alkanes via the hydrazone, which is commonly referred to as the Wolff−Kishner reaction.[1] Since the discovery of the Wolff−Kishner reduction almost a century ago, several modern variations (such as the Huang−Minlon modification) have been developed. In the case of α,β-unsaturated ketones and aldehydes, the transposition of the double bond was commonly the major reaction pathway, presumably through the intermediacy of an allylic diazene that underwent a [1,5]-sigmatropic rearrangement of hydrogen with the loss of nitrogen.[2] For most aromatic aldehydes and ketones, however, the major product was the unrearranged aromatic reduction product, either due to the intervention of another mechanistic pathway (such as a carbanion)[3] or due to rapid isomerization of the initial alicyclic isomer of the aromatic compound under the reaction conditions.[4] There are two notable exceptions to this generalization: Kishner's reduction of 2-furylhydrazone (**1**)[5] (Scheme 1) and the reduction of 3-furaldehyde employing the Huang−Minlon modification of the Wolff−Kishner reduction.[6] On the basis of chemical studies and the molecular refraction, Kishner proposed that the major product in the reduction of **1** catalyzed by platinized clay and potassium hydroxide was 2-methylene-2,3-dihydrofuran (**2**), although he could not rule out the possibility that the abnormal product was a mixture of **2** and 2-methylene-2,5-dihydrofuran (**3**). In his reinvestigation of Kishner's reduction of **1**, Rice[7] concluded that the major abnormal product was **3** based on UV−vis spectroscopy, since the absorption maximum of the isolated alicyclic isomer of 2-methylfuran was similar to other 1,3-diene compounds.

SCHEME 1. Kishner's Reduction of 2-Furylhydrazone



Our interest in Kishner's reduction of **1** arises from our related work with 3-methylene-2,3-dihydrofuran,[6] which we have found to be an excellent starting material for 3-substituted furans.[6,8] Given our successful utilization of 3-methylene-2,3-dihydrofuran, we reasoned that Kishner's abnormal reduction product would have potential as a starting material for the synthesis of 2-substituted furans. In our reinvestigation of Kishner's (and Rice's) work, we had two goals: conclusively establish the product(s) of the abnormal reduction by modern spectroscopic techniques and explore the reactivity of the abnormal reduction product, especially in the context of the ene reaction. We are unaware of any other reports in the literature concerning the abnormal reduction of 2-furylhydrazone (or 2-furaldehyde) or chemistry related to **2** or **3**.

Following the procedure described by Kishner and Rice with some minor modifications, we added the half hydrate of **1** to platinized clay and KOH. The major isolated products were 2-methylfuran and **2** (typical crude yield of **2** and 2-methylfuran was approximately 65%; 0.5−1:1 ratio of **2**/2-methylfuran), easily identified by ^1H and ^{13}C NMR. The ^1H NMR of abnormal reduction product **2** consists of four broad multiplets (one proton each) at δ 6.41, 5.12, 4.54 and 4.19, and an apparent pentet at δ 3.33 ($J = 2.7$ Hz) integrating for two protons. The ^{13}C NMR consists of five peaks at δ 161.7 (C), 144.5 (CH), 102.1 (CH), 83.8 (CH_2), and 32.7 (CH_2). The proton and carbon peaks of the methylene group were especially decisive in distinguishing between the two possible structures for the abnormal reduction product, since the expected chemical shifts for the methylene group in **3** would be substantially downfield from the observed chemical shifts. For example, the protons and carbons of the methylene groups of 2,5-dihydrofuran resonate at δ 4.63 and 75.4, respectively. The abnormal reduction

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(1) Todd, D. *Org. React.* **1948**, *4*, 378−422.

(2) Wood, J. L.; Porco, J. A., Jr.; Taunton, J.; Lee, A. Y.; Clardy, J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 5898−5900.

(3) Taber, D. F.; Stachel, S. J. *Tetrahedron Lett.* **1992**, *33*, 903−906.

(4) Milder methods for generating a benzylic diazene has led to the synthesis of alicyclic isomers of aromatic compounds. See: Myers, A. G.; Movassaghi, M.; Zheng, B. *J. Am. Chem. Soc.* **1997**, *119*, 8572−8573.

(5) (a) Kishner, N. *Zh. Obs. Khim.* **1931**, *1*, 1212−1228; *Chem. Abstr.* **1931**, *26*, 51393. (b) Kishner, N. *Zh. Obs. Khim.* **1933**, *3*, 198−200; *Chem. Abstr.* **1933**, *28*, 14046.

(6) Miles, W. H.; Berreth, C. L.; Smiley, P. M. *Tetrahedron Lett.* **1993**, *34*, 5221−5222.

(7) Rice, H. L. *J. Am. Chem. Soc.* **1952**, *74*, 3193−3194.

(8) Miles, W. H.; Berreth, C. L.; Anderton, C. A. *Tetrahedron Lett.* **1996**, *37*, 7893−7896. Miles, W. H.; Fialcowitz, E. J.; Halstead, E. S. *Tetrahedron* **2001**, *57*, 9925−9929. Miles, W. H.; Connell, K. B. *Tetrahedron Lett.* **2003**, *44*, 1161−1163.

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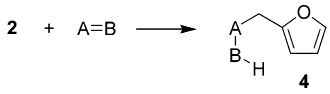
SCHEME 2. Reaction of 2 with Enophiles



product isolated in this study was clearly the same as the one isolated by Rice: the boiling point was nearly identical (bp 75−76 °C (lit.[7] bp 76.5−77 °C)) and the UV−vis was identical ($\lambda_{max} = 239$ nm; $\epsilon_{max} = 6800$). In addition to 2-methylfuran and **2**, we did observe small, variable quantities (1−5%) of another product in the distillate whose ^{1}H NMR (δ 6.30 (m, 1H), 6.17 (m, 1H), 4.94 (m, 1H), 4.23 (m, 1H), and 3.94 (m, 2H)) was consistent with abnormal product **3**, but we were unable to isolate the compound in sufficient quantity or purity to make a definitive assignment of structure. The separation of **2** and 2-methylfuran was extremely difficult and resulted in significant loss of **2**, but we found that mixtures of **2** and 2-methylfuran were entirely satisfactory for our synthetic studies.

The alicyclic isomers of aromatic compounds have enormous potential as a partner in the ene reaction[9,10] (Scheme 2) due to the stability of the resulting aromatic product.[6,8,11] As expected, **2** was very reactive in some of the examined ene reactions, but less reactive than 3-methylene-2,3-dihydrofuran. The reaction of **2** (containing 2-methylfuran) with representative enophiles is summarized in Table 1. The carbonyl-ene reaction of **2** with electron-poor ethyl glyoxalate occurred rapidly at 0 °C to give alcohol **4a** in 89% yield (entry 1). The Lewis acid-catalyzed reaction of **2** with benzaldehyde (Yb(fod)$_3$; entry 2) and decanal (ZnCl$_2$; entry 4) gave good yields of the corresponding racemic alcohols **4b** and **4c**. Most gratifying was the asymmetric carbonyl-ene reaction of **2** with benzaldehyde (entry 3) and decanal (entry 5) using a Ti(OCH(CH$_3$)$_2$)$_4$/(*S*)-BINOL catalyst,[9,12] giving the nonracemic alcohols (*S*)-**4b** and (*R*)-**4c** in 54% ee and 94% ee, respectively. Using Yb(fod)$_3$ as a catalyst, **2** reacted with 2,3-*O*-isopropylidene-D-glyceraldehyde to give alcohol **4d** in moderate diastereoselectivity (entry 6). Eschenmoser's salt reacted rapidly with **2** to give amine salt **4e** (entry 7). The successful carbonyl-ene reactions of **2** stand in contrast to the reactions of alkenyl enophiles with **2**; the reaction of **2** with most alkenes was slow and unsuccessful. In the case of diethyl maleate and **2** (entry 8), we obtained ene product **4f** in 56% yield after heating in a sealed tube for 65 h at 150−160 °C. Maleic anhydride,[5a] diethyl fumarate, and ethyl acrylate gave low yields or no yield of the corresponding ene product. We briefly explored Lewis acids suitable for the ene reaction of **2** with alkenyl enophiles, but the rapid isomerization and/or decomposition of **2** under these conditions precluded their use as catalysts.

We also reinvestigated the reaction of **2** with excess 1,4-benzoquinone (Scheme 3), which Kishner reported in a follow-up paper[5b] as giving a red solid with a 1:2 stoichiometry of **2** and 1,4-benzoquinone. Following Kishner's procedure, we obtained a brick-red solid with a melting point comparable to the melting point reported by Kishner. The spectroscopic data for the red solid were consistent with electron donor−acceptor complex **6** consisting of 1:1 product **5** and 1,4-benzoquinone. The spectroscopic data ruled out the expected ene product **7** and the tautomeric 2-substituted hydroquinone **8** as the 1:1 product. The mono-alkylated 1,4-hydroquinone subunit was firmly established by the AA′BB′ pattern in the ^{1}H NMR (δ 7.01 and 6.47, 4 H), an exchangeable proton at δ 4.14, and four peaks in the ^{13}C NMR at δ 151.9 (C), 151.3 (C), 119.0 (CH) and 116.1 (CH). The protons of exocyclic alkenyl subunit appear as two broad singlets at δ 4.56 and 4.00, and the carbons appear at δ 162.7 (C) and 84.7 (CH$_2$). The other alkenyl protons have chemical shifts (δ 5.85 and 5.68) and a coupling constant (J = 5.9 Hz), consistent with a double bond in the 3,4 position of a 2,5-dihydrofuran. The sp^3 carbon (δ 107.7) and its associated proton (δ 6.14) were suggestive of the acetal moiety. Column chromatography of **6** gave 1,4-benzoquinone (63% yield) and impure **5** (76% yield), an air- and thermally sensitive oil. The reaction of equimolar quantities of **2** and 1,4-benzoquinone gave impure **5** in low yields. A mechanism for this reaction would be highly speculative at this time, but would have to account for the formation of another alicyclic furanyl moiety instead of a thermodynamically more stable aromatic furan product.

In conclusion, we have unequivocally identified the major abnormal reduction product of **1**, using Kishner's conditions, as the alicyclic isomer **2**. This study demonstrates that **2** has excellent potential as a reagent in the carbonyl-ene reaction, thus serving as a starting material for a wide variety of 2-substituted furans.[13,14] Since **2** is functionally equivalent to the difficult-to-prepare 2-(metallomethyl)furan reagents, the chemistry of alicyclic isomer **2** offers a nice solution to a long-standing problem. The manipulation of the furan ring[15,16] also provides ready access to a variety of functionality, so **2** may offer an important entry point for synthesis of many diverse compounds. The reaction conditions for the synthesis of

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(9) For reviews, see: Dias, L. C. *Curr. Org. Chem.* **2000**, *4*, 305−342. Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021−1050.

(10) For recent advances, see: Alcaide, B.; Almendros, P.; Pardo, C.; Rodríguez-Ranera, C.; Rodríguez-Vicente *J. Org. Chem.* **2003**, *68*, 3106−3111. Williams, J. T.; Bahia, P. S.; Snaith, J. S. *Org. Lett.* **2002**, *4*, 3727−3730. Okachi, T.; Fujimoto, K.; Onaka, M. *Org. Lett.* **2002**, *4*, 1667−1669.

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(13) For a review of furan chemistry, see: Hou, X. L.; Cheung, H. Y.; Hon, T. Y.; Kwan, P. L.; Lo, T. H.; Tong, S. Y.; Wong, H. N. C. *Tetrahedron* **1988**, *54*, 1955−2020.

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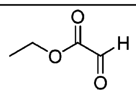
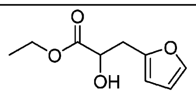
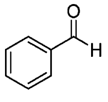
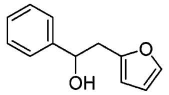
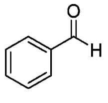
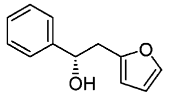
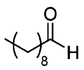
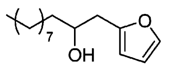
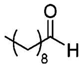
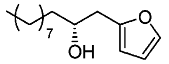
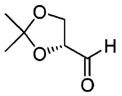
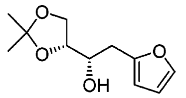
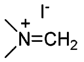
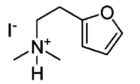
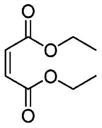
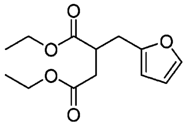
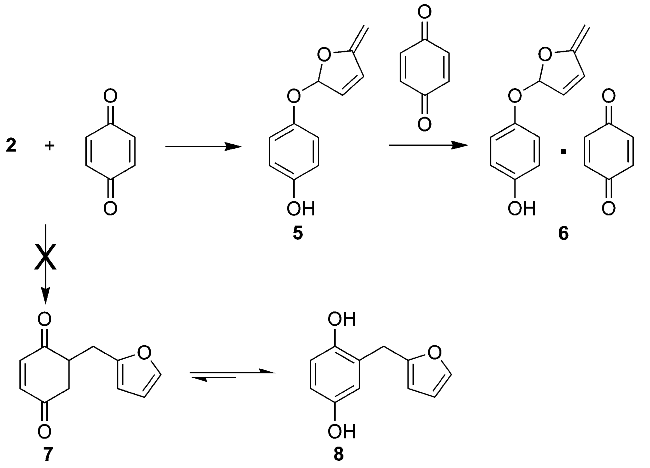
(16) For recent applications, see: Padwa, A.; Brodney, M. A.; Lynch, S. M.; Rashatasakhon, P.; Wang, Q.; Zhang, H. *J. Org. Chem.* **2004**, *69*, 3735−3745. Hughes, C. C.; Kennedy-Smith, J. J.; Trauner, D. *Org. Lett.* **2003**, *5*, 4113−4115. Trost, B. M.; Yeh, V. S. C. *Org. Lett.* **2002**, *4*, 3513−3516. Arjona, O.; Menchaca, R.; Plumet, J. *Org. Lett.* **2001**, *3*, 107−109.

TABLE 1. Reaction of 2 with Enophiles

Entry	Substrate	Conditions (Temp; solvent; catalyst)	Product	Yield (%) [% ee or de]
1		0^{0}C; CH$_2$Cl$_2$; none	 **4a**	89
2		22^{0}C; Et$_2$O/CH$_2$Cl$_2$; Yb(fod)$_3$	 **4b**	96
3		22^{0}C; Et$_2$O; Ti(IV)/(*S*)-BINOL	 **(*S*)-4b**	91 [54]
4		22^{0}C; CH$_2$Cl$_2$; ZnCl$_2$	 **4c**	78
5		22^{0}C; Et$_2$O; Ti(IV)/(*S*)-BINOL	 **(*R*)-4c**	65 [94]
6		0^{0}C; CH$_2$Cl$_2$; Yb(fod)$_3$	 **4d**	93 [65]
7		22^{0}C, CH$_2$Cl$_2$; none	 **4e**	74
8		150-160^{0}C; *m*-xylene; none	 **4f**	56

SCHEME 3. Reaction of 2 with 1,4-Benzoquinone



2, however, are particularly violent, not amendable to small scale, and gives relatively low yields of **2**. Our attempts to prepare **2** on a smaller scale by alternative methodologies (reduction of 2-furyltosylhydrazone[17] or reductive allylic transposition of furfuryl alcohol[4]) have so far failed, giving only 2-methylfuran and unidentified products. We are continuing to explore alternative preparations of **2** and to delineate the synthetic potential of **2** (and related compounds), which will be reported in due time.

Experimental Section

2-Furylhydrazone (1). Caution: Even though we prepared **1** several times by the following method (or with minor variations) during this study with no problems, one distillation became explosively violent while we were distilling off the excess hydrazine at atmospheric pressure, releasing a plume of yellow smoke and charred organic material. The receiving flask contained **2** and 2-methylfuran, so we believe the unexpected exothermic decomposition was caused by a contaminant (either base or transition metal) that catalyzed the decomposition of **1**. We believe the following measures will minimize the likelihood of such a problem: washing the distillation flask with acid to remove basic or transition metal contaminants, using an oil bath (rather than a heating mantel that may have "hot spots") for greater control of the temperature, and distilling the water and excess hydrazine under a partial vacuum. Doing the distillation

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[17] Kabalka, G. W.; Summers, S. T. *J. Org. Chem.* **1981**, *46*, 1217–1218.

in smaller batches also may mitigate a potentially violent situation. 2-Furaldehyde (300 mL, 348 g 3.62 mol) was added to $NH_2NH_2{\cdot}H_2O$ (600 mL, 619 g, 12.4 mol) over 30 min with a water bath to moderate the resulting exothermic reaction. After stirring at ambient temperature for 0.5 h, 50 g of sodium carbonate was added. The liquid phase was decanted from the sodium carbonate. The crude reaction mixture was distilled at atmospheric pressure, then under a partial vacuum (100 mm) to remove the water and excess hydrazine, and finally distilled under vacuum (0.1 mm, bp 90−105 °C) to give **1** as an oil (263 g, 66% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.39 (br d, J = 1.1 Hz, 1H), 6.43 (d, J = 3.3 Hz, 1H), 6.39 (dd, J = 1.8, 3.7 Hz, 1H), 5.55 (br s, 2H).

2-Methylene-2,3-dihydrofuran (2). The following is a typical run for the preparation of **2**, following the procedure described by Kishner[5a] and Rice.[7] Moist potter's clay (1.5 g) was placed in a 25 mL Schlenk flask with a magnetic stirring bar. A 2.5% H_2PtCl_6 solution (3 mL) was added and stirred until the mixture was homogenized. The catalyst was dried at 100 °C for 1 h with a gentle stream of air passing over it. A balloon of H_2 was put on the reaction vessel, and the catalyst was heated to 150 °C for 2 h. After the reaction vessel had cooled to room temperature, the hydrogen balloon was replaced with a balloon of CO_2. The catalyst and KOH (1.5 g) were then placed in a 500 mL three-neck RB flask, which had been previously flushed with Ar, fitted with a dropping funnel, a distillation apparatus in which the receiving vessel was cooled in dry ice/acetone, and a stopper. The distillation apparatus was connected to a trap that also was cooled in dry ice/acetone. The reaction vessel was heated to 130 °C with an oil bath, and 5−10 mL portions of 2-furylhydrazone-half hydrate (281 g, 2.39 mol) were added. The decomposition of **1**, especially during the addition of the first two or three portions, was extremely violent, leading to the loss of some product even with the cooling system described. The oil bath temperature was increased in order to induce the rapid decomposition of **1**; slow decomposition invariably meant poor selectivity for **2**, with almost exclusive formation of 2-methylfuran. As the addition progressed, the oil bath temperature was raised to 210−220 °C. Under these conditions, the amount of **1** added in each portion was limited by the associated foaming. The combined collected distillate was washed with 2% Na_2CO_3 (200 mL), water (2 × 200 mL), and brine (200 mL) and then dried over Na_2CO_3. The crude product (165 g; approximately 1:1.4 **2**/2-methylfuran; 35% crude yield of **2**) was distilled under Ar at atmospheric pressure to give six fractions: fraction 1 (54−65 °C; 31.1 g, 1:5 **2**/2-methylfuran), fraction 2 (65−67 °C; 21.5 g, 1:4 **2**/2-methylfuran), fraction 3 (67−68 °C; 23.8 g, 1:3 **2**/2-methylfuran), fraction 4 (68−74 °C; 38.0 g, 1.3:1 **2**/2-methylfuran), fraction 5 (74−75 °C; 20.2 g, 4:1 **2**/2-methylfuran), and fraction 6 (75−76 °C; 9.8 g, 10:1 **2**/2-methylfuran); IR (CH_2Cl_2) 1680, 1622 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.41 (m, 1H), 5.12 (m, 1H), 4.54 (m, 1H), 4.19 (m, 1H), 3.33 (app pentet, J = 2.7 Hz, 2H); ^{13}C NMR (100 MHz) 161.7 (C), 144.5 (CH), 102.1 (CH), 83.8 (CH_2), 32.7 (CH_2); UV−vis (λ_{max} = 239 nm, ϵ = 6800, after correcting for purity as determined by ^1H NMR). The signals associated with 2-methylfuran resonated at δ 7.27, 6.41, 5.96, and 2.29 in the ^1H NMR and δ 152.1, 140.7, 110.3, 105.4, and 13.4 in the ^{13}C NMR. The use of kaolin instead of moist potter's clay gave similar yields of **2**. Smaller scale reactions gave lower yields (20−30%) of **2.** When mixtures of **2** and 2-methylfuran were stored over potassium carbonate in the freezer for several months, there was slow isomerization of **2**, with fractions containing a high proportion (>90%) of **2** undergoing more rapid isomerization.

(±)-2-(2-Furyl)-1-phenylethan-1-ol[18] (4b; Entry 2, Table 1). To a solution of benzaldehyde (0.250 mL, 0.261 g, 2.46 mmol) in CH_2Cl_2 (2 mL) were added **2** (1.0 mL of a 1:2 mixture of **2**/2-methylfuran, approximately 3.7 mmol of **2**), $NaHCO_3$ (0.050 g, 0.60 mmol), and Yb(fod)$_3$ (0.132 g, 0.125 mmol). After stirring for 18 h, the reaction mixture was transferred to a separatory funnel with CH_2Cl_2 (10 mL) and H_2O (10 mL). The organic phase was separated, and the aqueous was extracted with additional CH_2Cl_2 (10 mL). The combined organic phases were washed with brine (10 mL) and dried over Na_2SO_4, and the volatiles were removed on a rotary evaporator. The crude product was purified by flash chromatography (25 g silica gel; 10% ethyl acetate in hexanes) to give **4b** (0.443 g, 96% yield) as a yellow oil: IR 3400, 1600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27−7.40 (m, 6H), 6.32 (dd, J = 1.8, 2.9 Hz, 1H), 6.09 (d, J = 3.3 Hz, 1H), 5.03 (dt, J = 1.8, 6.6 Hz, 1H), 3.08 (d, J = 6.6 Hz, 2H), 2.47 (br s, 1H); ^{13}C NMR (100 MHz) δ 152.3, 143.3, 141.6, 128.4, 127.6, 125.7, 110.3, 107.3, 72.8, 38.2.

(*R*)-1-(2-Furyl)undecan-2-ol ((*R*)-4c; Entry 5, Table 1). To 4 Å molecular sieves (0.50 g) in ether (10 mL) were added (*S*)-1,1′-bi-2-naphthol (0.286 g, 0.998 mol) and titanium(IV) isopropoxide (0.143 mL, 0.138 g, 0.484 mmol). The reaction mixture was refluxed for 1 h and was allowed to cool to room temperature. Decanal (0.94 mL, 0.78 g, 5.0 mmol) was added, the mixture was stirred for 5 min, and **2** (1.30 mL of a 1.3:1 mixture of **2**/2-methylfuran, approximately 8.2 mmol of **2**) was added over 5 min. The reaction mixture was stirred at room temperature for 15 min. Saturated sodium bicarbonate solution (1 mL) was added, and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was filtered through a Celite bed, which was washed with additional ether (75 mL). The ether solution was washed with 1.0 M NaOH (2 × 60 mL) and dried over Na_2SO_4, and the volatiles were removed on the rotary evaporator. The crude product was purified by flash chromatography (60 g of silica gel; 10% ethyl acetate in hexanes) to give (*R*)-**4c** (0.781 g, 65% yield; 94% ee) as a white solid: mp 35−36 °C; IR 3443, 1642 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 1.4 Hz, 1H), 6.30 (dd, J = 2.0, 3.1 Hz, 1H), 6.10 (d, J = 2.9, 1H), 2.84 (dd, J = 4.0, 15.0 Hz, 1H), 2.71 (dd, J = 8.1, 15.0 Hz, 1H), 1.78 (d, J = 4.0 Hz, 1H), 1.47 (m, 2H), 1.26 (br s, 14H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 141.6, 110.3, 107.0, 70.5, 36.7, 36.1, 31.9, 29.57 (2 C), 29.53, 29.3, 25.6, 22.7, 14.1. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.53; H, 11.20. The enantiomeric excess was determined by the use of the chiral shift reagent Eu(hfc)$_3$. The methine proton bonded to the carbon adjacent to the hydroxy group for the two enantiomers resonates as broad singlets at δ 6.06 for (*R*)-**4c** and δ 5.86 for (*S*)-**4c** (0.10 M of **4c** with 33 mol % Eu(hfc)$_3$ in $CDCl_3$). The assignment of the absolute stereochemistry of the major enantiomer in this reaction was based on the comparison of the ^1H NMR spectra of the (+)-MTPA esters of **4c** and the structurally similar (+)-MTPA esters of 2-methyl-1-nonen-4-ol.[19] The alkenyl protons of (+)-MTPA ester of (*R*)-2-methyl-1-nonen-4-ol resonated downfield (δ 4.83 and 4.76) from the (+)-MTPA ester of (*S*)-2-methyl-1-nonen-4-ol (δ 4.72 and 4.65). The ^1H NMR spectra of the (+)-MTPA ester of the major enantiomer of the above reaction resonates at δ 6.29 (dd, 1H, J = 2.0, 3.1 Hz) and 6.07 (d, 1H, J = 2.9 Hz, H_3), downfield from the minor isomer at δ 6.22 (dd, 1H, J = 2.0, 3.1 Hz) and 5.53 (d, 1H, J = 2.9 Hz, H_3).

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Supporting Information Available: Experimental details and characterization data for **4**−**6**; copies of ^1H and ^{13}C NMR for **2** and **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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