

Diethyl tartrate was compared to diisopropyl tartrate to examine the effect of the steric bulk of the chiral tartrate ligand on the enantioselectivity of the oxidation. Diisopropyl tartrate was found to be slightly superior, increasing the ee by 5% at 60% reaction completion (Table III).

Kinetic resolution of other racemic sulfides by this method should be possible when one considers the substrate diversity reported for the asymmetric sulfoxide formation.<sup>3</sup>

### Experimental Section

**General Methods.** Compounds 3 and 4 were prepared by published procedures.<sup>6,7</sup> Toluene and dichloromethane were distilled from calcium hydride. Titanium tetrakisopropoxide, (+)-diisopropyl tartrate, and (+)-diethyl tartrate were distilled under high vacuum. The *t*-Bu hydroperoxide in isooctane was obtained from Aldrich and titrated.<sup>1c</sup> Pellet 4-Å molecular sieves obtained from Red Bird Service were activated by heating in a vacuum oven at 110 °C for at least 16 h. Silica gel 60 (finer than 230 mesh) was obtained from E. Merck and activated by heating under vacuum at 50 °C for 4 h. Preparative chromatography was performed on a Waters Associates Prep LC/System 500A. NMR spectra were obtained at 300 MHz. Trifluoroanethylethanol was obtained from Aldrich.

**5-[[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-methyl]-2-thioxo-4-thiazolidinone (5).** To a stirred suspension of **3**<sup>6</sup> (41.94 g, 120 mmol) in toluene (1.8 L) was added diethyl 2,6-dimethyl-1,4-dihydro-3,5-pyridinedicarboxylate (**4**)<sup>7</sup> (39.51 g, 156 mmol) and activated silica gel 60 (120 g). The mixture was heated to 80 °C for 22 h, and then the warm suspension was filtered. The filter cake was rinsed with ethyl acetate. The combined filtrate and rinse were evaporated to dryness. The evaporation residue was redissolved in ethyl acetate and extracted with five portions of 1 N HCl. The ethyl acetate layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to yield **5** (42.6 g, 100%) as a yellow solid: mp 178–179 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 9.05 (s, 1 H), 7.03 (s, 2 H), 5.22 (s, 1 H), 4.58 (dd, *J* = 3, 9 Hz, 1 H), 3.51 (dd, *J* = 3, 15 Hz, 1 H), 3.09 (dd, *J* = 9, 15 Hz, 1 H), 1.45 (s, 18 H); FD MS 351 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>NO<sub>2</sub>S<sub>2</sub>: C, 61.50; H, 7.17; N, 3.98. Found: C, 61.60; H, 7.21; N, 4.14.

**5-[[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-methyl]-4-thiazolidinone (6).** Hydrogenation of **5** (32.3 g, 92 mmol) in EtOH (2.3 L) in the presence of 5% Pd/C (110 g) under 500 psi of H<sub>2</sub> for 20 h at 120 °C yielded, after filtration and evaporation of solvent, crude **6**. Crystallization with CH<sub>2</sub>Cl<sub>2</sub> and trituration with hot hexane resulted in pure **6** (14.6 g, 49.5% yield) as white crystals: mp 149–152 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.16 (s, 1 H), 7.11 (s, 2 H), 5.15 (s, 1 H), 4.25 (d, *J* = 9 Hz, 1 H), 4.07 (d, *J* = 9 Hz, 1 H), 3.93 (dd, *J* = 3, 6 Hz, 1 H), 3.35 (dd, *J* = 3, 14 Hz, 1 H), 2.93 (dd, *J* = 6, 14 Hz, 1 H), 1.4 (s, 18 H); FD MS 321 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>27</sub>NO<sub>2</sub>S: C, 67.25; H, 8.47; N, 4.36. Found: C, 67.05; H, 8.54; N, 4.61.

**(-)-5-[[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-methyl]-4-thiazolidinone [(–)6].** To a stirred suspension of 4-Å molecular sieves (1.05 g) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) were added titanium tetrakisopropoxide (0.45 mL, 1.5 mmol), (+)-diisopropyl tartrate (0.63 mL, 3.0 mmol), and deionized water (27 μL, 1.5 mmol), respectively. The suspension was allowed to stir at rt for 20 min before addition of thiazolidinone (±)-**6** (0.80 g, 2.5 mmol). After dissolution of the sulfide, the reaction was cooled to –20 °C and 2.57 M *t*-Bu hydroperoxide solution in isooctane (0.58 mL, 1.5 mmol) was added. The reaction was stirred at –20 °C for 6 h, at which time the molecular sieves were removed by filtration. The filtrate was quenched by pouring into a stirred 50-mL solution prepared from citric acid monohydrate (3.3 g), ferrous sulfate heptahydrate (9.9 g), and deionized water. Stirring was continued for 30 min, and then the layers were left to separate. The aqueous layer was extracted with an equal volume of CH<sub>2</sub>Cl<sub>2</sub>. The original CH<sub>2</sub>Cl<sub>2</sub> layer and the CH<sub>2</sub>Cl<sub>2</sub> extract were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent followed by NMR analysis of a CDCl<sub>3</sub> solution of the residue showed a 40/60 ratio of **6** to its sulfoxide products, **7** (80/20 mixture of diastereomers). The evaporation residue was chromatographed on silica gel. Elution with 6 L of a 10%–50% ethyl acetate in hexane gradient yielded (–)-**6** (0.29 g, 36% recovery) as a white foam: mp 144–146

°C; [α]<sub>D</sub><sup>20</sup> –56.99° (c 1.0, MeOH). Anal. Calcd for C<sub>18</sub>H<sub>27</sub>NO<sub>2</sub>S: C, 67.25; H, 8.47; N, 4.36. Found: C, 67.31; H, 8.55; N, 4.12.

When the reaction was taken to 70% completion using (–)-diisopropyl tartrate (+)-**6** was recovered as a white foam: mp 144–146 °C; [α]<sub>D</sub><sup>20</sup> +70.41° (c 1.0, MeOH); ee 84% (HPLC). Anal. Calcd for C<sub>18</sub>H<sub>27</sub>NO<sub>2</sub>S: C, 67.25; H, 8.47; N, 4.36. Found: C, 66.95; H, 8.22; N, 4.26.

**5-[[3,5-Bis(1,1-dimethylethyl)-4-hydroxyphenyl]-methyl]-4-thiazolidinone 1-Oxide (7).** Continued elution of the silica gel column with 4 L of 50% 2-propanol in hexane yielded **7** (0.46 g, 55%). Isomer A: mp 182–184 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.02 (s, 2 H), 6.02 (s, 1 H), 5.23 (s, 1 H), 4.05 (dd, *J* = 3, 12 Hz, 1 H), 3.63 (m, 2 H), 3.37 (dd, *J* = 5, 14 Hz, 1 H), 3.09 (dd, *J* = 8, 14 Hz, 1 H), 1.43 (s, 18 H); FD MS 337 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>27</sub>NO<sub>3</sub>S: C, 64.06; H, 8.06; N, 4.15. Found: C, 63.84; H, 8.09; N, 4.12. Isomer B: mp 177–181 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.16 (s, 2 H), 7.04 (s, 1 H), 5.19 (s, 1 H), 4.32 (s, 2 H), 3.46 (dd, *J* = 3, 12 Hz, 1 H), 3.37 (dd, *J* = 3, 15 Hz, 1 H), 3.17 (dd, *J* = 12, 15 Hz, 1 H), 1.45 (s, 18 H); FD MS: 337 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>27</sub>NO<sub>3</sub>S: C, 64.06; H, 8.06; N, 4.15. Found: C, 63.88; H, 8.12; N, 4.29.

**Determination of Enantiomeric Excess.** Two methods were used to determine the ee of the resolved thiazolidinone **6**. HPLC on a Chiracel OJ column using 15% 2-propanol in hexane as mobile phase results in *t*<sub>R</sub> = 4.9 min for (–)-**6** and *t*<sub>R</sub> = 5.8 min for (+)-**6** using 280-nm UV detection. NMR spectroscopy of a CDCl<sub>3</sub> solution of **6** treated with the chiral shift reagent trifluoroanethylethanol results in an enantioselective shifting of the peak at δ 4.25. Good agreement of these two methods was seen in all cases (see tables).

### Syn/Anti Diastereoselectivity in the Reduction of α-Alkoxy Ketones by Tin Hydride Reagents

Ikuya Shibata,\* Tomoyuki Yoshida, Takayo Kawakami, Akio Baba, and Haruo Matsuda

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

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The general problem of the stereocontrolled construction of acyclic materials has been a topic of intensive investigation. In recent years, considerable progress has been made in controlling the stereochemistry of the reaction of α-alkoxy carbonyl compounds by the interaction between an alkoxy group and Lewis acids.<sup>1</sup> Organotin compounds such as allylstannane play an important role in controlling the diastereoselectivity by the assistance of Lewis acids.<sup>2</sup>

In the reduction of α-alkoxy ketones, the selection of reducing agent to control the diastereoselectivity is difficult. Generally, the control is achieved by using oxygen substituents.<sup>3</sup> Fujita and Hiyama have reported unique reducing systems using silyl hydrides to control the diastereoselectivity for a single substrate.<sup>4</sup> However, the selectivity in such reactions using organotin hydrides has not been reported because of their radical manner.<sup>5</sup> We

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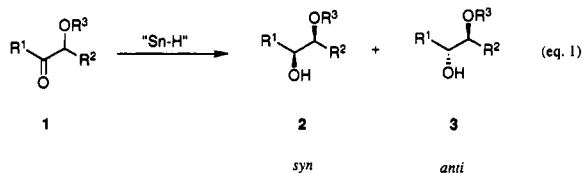
**Table I. Diastereoselective Reduction of Alkoxy Ketones by Tin Hydride Systems<sup>a</sup>**

entry	substrate	reducing system	conditions	yield (%) <sup>b</sup>	2:3 <sup>c</sup>
1		Bu <sub>3</sub> SnH	60 °C, 24 h	16	43:57
2		Bu <sub>3</sub> SnH-HMPA	60 °C, 24 h	30	54:46
3		Bu <sub>3</sub> SnH-Bu <sub>4</sub> NCl	rt, 24 h	92	69:31
4		Bu <sub>3</sub> SnH-Bu <sub>4</sub> NF	0 °C, 5 h	81	100:0
5		Bu <sub>2</sub> SnClH	0 °C, 5 h	72	10:90
6		Bu <sub>3</sub> SnH-Bu <sub>4</sub> NF	0 °C, 5 h	70	65:35
7		Bu <sub>2</sub> SnClH	0 °C, 2 h	100	10:90
8		Bu <sub>3</sub> SnH-Bu <sub>4</sub> NF	0 °C, 6 h	73	99:1
9		Bu <sub>2</sub> SnClH	0 °C, 4 h	40	25:75
10		Bu <sub>3</sub> SnH-Bu <sub>4</sub> NF	0 °C, 5 h	71	74:26
11		Bu <sub>2</sub> SnClH	0 °C, 2 h	62	9:91
12		Bu <sub>3</sub> SnH-Bu <sub>4</sub> NF	0 °C, 5 h	80	91:9 <sup>d</sup>
13		Bu <sub>2</sub> SnClH	0 °C, 4 h	56	31:69 <sup>d</sup>

<sup>a</sup> Substrate 2 mmol, tin hydride 2 mmol, additive 2 mmol.  
<sup>b</sup> Isolated yield. <sup>c</sup> Determined by <sup>1</sup>H NMR. <sup>d</sup> Cis:trans.

have reported the novel use of Bu<sub>3</sub>SnH as a hydride source by using additives such as HMPA<sup>6</sup> and tetra-*n*-butylammonium halides (*n*-Bu<sub>4</sub>NX, X = halogen).<sup>7</sup> These Lewis bases coordinate the tin atom and increase the reducing ability of Bu<sub>3</sub>SnH.

Herein we present a study of the reduction of  $\alpha$ -alkoxy ketones using organotin hydride reagents (eq 1). This



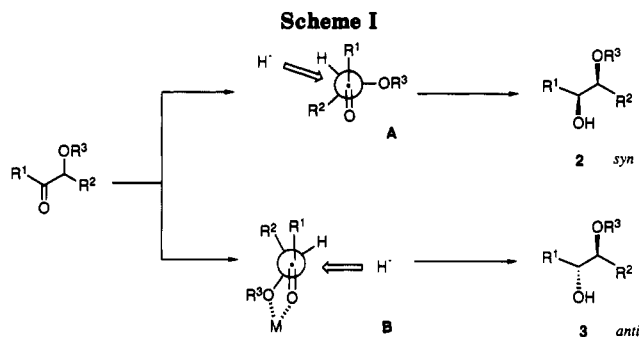
report describes a dependency of the diastereoselectivity on the selection of the tin hydride system. These tin hydride reductions have several advantages. They proceed under mild and neutral conditions,<sup>8</sup> and the products, tin alkoxides, are easily protonated by MeOH quench to form the corresponding alcohols.

Reductions of **1a** to the alcohols **2a** and **3a** were initially examined with a variety of tin hydride reagents and the results are presented in Table I. Reduction with Bu<sub>3</sub>SnH alone gave the product in only 16% yield (entry 1). Bu<sub>3</sub>SnH-HMPA increased the yield of the product (entry 2). However, the reaction was not diastereoselective at all. In contrast, the use of ammonium halides such as *n*-Bu<sub>4</sub>NCl and *n*-Bu<sub>4</sub>NF resulted in efficient reducing systems (entries 3 and 4). The reaction proceeded in good yields; moreover, syn selectivity of the product was greatly increased. Noteworthy is that the alcohol obtained by

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(8) In the reaction of allylstannanes, strong Lewis base such as BF<sub>3</sub>·OEt<sub>2</sub> and TiCl<sub>4</sub> were to control the diastereoselectivity.<sup>2</sup>

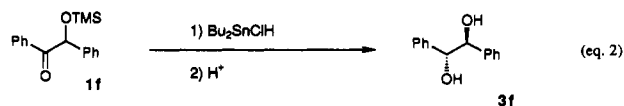


using the Bu<sub>3</sub>SnH-Bu<sub>4</sub>NF system was only the syn isomer (entry 4). The products are stable to the reaction conditions. Namely, after stirring the reaction mixture in entry 4 at room temperature for 2 h, the yield and the diastereoselectivity were not changed at all. As shown in Scheme I, this syn-selective reaction is explained in terms of the Felkin-Ahn model A in which interaction of carbonyl oxygen with a counter cation is ideally suppressed because of the coordination of a Lewis base with the tin atom.<sup>9</sup> Thus the Bu<sub>3</sub>SnH-Bu<sub>4</sub>NF system provided syn selective reduction.

Contrary to the above syn-selective reduction, an anti-selective reaction could be performed by using Bu<sub>2</sub>SnClH, which is easily prepared by redistribution of Bu<sub>2</sub>SnH<sub>2</sub> and Bu<sub>2</sub>SnCl<sub>2</sub>.<sup>10</sup> The reaction of **1a** afforded anti alcohol **3a** in 90% selectivity (entry 5).<sup>11</sup> The yield and the selectivity were not changed even after 2 h at room temperature. In this reaction, transition state B, which predicts the anti selectivity, should be favored over A.<sup>12</sup>

In this way, control of the syn and anti selectivity could be established with Bu<sub>3</sub>SnH-Bu<sub>4</sub>NF and Bu<sub>2</sub>SnClH, respectively. These reducing systems could be also applied to other substrates as shown in Table I. In the reaction of benzoin methyl ether (**1b**), syn selectivity was increased with the Bu<sub>3</sub>SnH-Bu<sub>4</sub>NF system (entry 6). In contrast, anti control could be successfully established by using Bu<sub>2</sub>SnClH (entry 7). Compared with **1b**, isobutyl ether (**1c**) gave increased syn isomer selectivity (entry 8). This is because of the steric bulkiness of the isopropyl group which prevents the chelation intermediate B. In the reduction of a methyl ketone such as **1d**, the diastereoselectivity was also changed (entries 10 and 11). The diastereoselective reduction found further applications in cyclic substrate **1e**. Cis and trans selectivity of the products was changed with the presented tin hydride systems (entries 12 and 13).

In the reduction of  $\alpha$ -siloxy ketone **1f**, using Bu<sub>2</sub>SnClH resulted in an anti-selective reaction. Because **1f** bears a removable group on the alkoxy group, desilylation occurred during workup and product **3f** was obtained in 90% yield (eq 2).



In conclusion, control of diastereoselectivity in the reduction of  $\alpha$ -alkoxy ketones could be performed with organotin hydride systems such as Bu<sub>3</sub>SnH-Bu<sub>4</sub>NF and Bu<sub>2</sub>SnClH.

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### Experimental Section

Melting points are uncorrected.  $^1\text{H}$  NMR spectra were recorded at 90 or 400 MHz. Analytical GC was performed using a 2-m  $\times$  3-mm glass column packed with Silicone OV-17 on Uniport HP (5%, 60–80 mesh) or a 25-m  $\times$  0.25-mm capillary column packed with CBP-10. Column chromatography was performed on silica gel (Wakogel C-200 or C-300). Preparative TLC was carried out on silica gel plates (Wakogel B-5F).

Tri-*n*-butyltin hydride ( $\text{Bu}_3\text{SnH}$ ) was synthesized by the reduction of tri-*n*-butyltin chloride ( $\text{Bu}_3\text{SnCl}$ ) with  $\text{LiAlH}_4$ . Chlorodi-*n*-butyltin hydride ( $\text{Bu}_2\text{SnClH}$ ) was synthesized by the redistribution reaction from di-*n*-butyltin dihydride ( $\text{Bu}_2\text{SnH}_2$ ) and di-*n*-butyltin dichloride ( $\text{Bu}_2\text{SnCl}_2$ ).<sup>10</sup>  $\text{Bu}_2\text{SnH}_2$  was obtained by a similar preparation of  $\text{Bu}_3\text{SnH}$ .

$\alpha$ -Alkoxy ketones **1a** and **1d** were synthesized by alcoholysis of the corresponding silyl enol ethers in the presence of iodosobenzene.<sup>13</sup> Benzoin ethers **1b** and **1c** and cyclic compound **1e** were commercially available.  $\alpha$ -Siloxy ketone **1f**<sup>14</sup> was prepared by silylation of benzoin with  $\text{Me}_3\text{SiCl-Et}_3\text{N}$ .<sup>15</sup>

**Representative Procedure for Syn-Selective Reductions Using  $\text{Bu}_3\text{SnH-Bu}_4\text{NF}$ .** A solution of 0.58 g (2 mmol) of  $\text{Bu}_3\text{SnH}$  in THF (2 mL) was stirred and cooled at 0 °C under  $\text{N}_2$ .  $\text{Bu}_4\text{NF}$  (2 mmol; 1 M THF solution) and 0.33 g (2 mmol) of **1a** were added. Stirring was continued for 5 h. After quenching with MeOH (5 mL), the solvent was removed under reduced pressure. The residue was subjected to column chromatography with hexane-EtOAc (1:1) to give **2a**<sup>16</sup> as a colorless oil (0.269 g, 81%). Identification of products was performed by  $^1\text{H}$  NMR and IR spectroscopy.

**Representative Procedure for Anti-Selective Reductions Using  $\text{Bu}_2\text{SnClH}$ .** To the solution of 0.24 g (1 mmol) of  $\text{Bu}_2\text{SnH}_2$  in THF (2 mL) was added 0.31 g (1 mmol) of  $\text{Bu}_2\text{SnCl}_2$  under  $\text{N}_2$ . The mixture was stirred at rt for 10 min. The IR band at 1820  $\text{cm}^{-1}$  due to the Sn-H bond of  $\text{Bu}_2\text{SnH}_2$  changed to 1850  $\text{cm}^{-1}$ , which indicated the formation of  $\text{Bu}_2\text{SnClH}$ . Ketone **1a** (0.61 g, 2 mmol) was added and this solution was stirred at 0 °C for 5 h. After quenching with MeOH (5 mL), the solvent was removed under reduced pressure. The residue was subjected to column chromatography with hexane-EtOAc (1:1) to give a 1:9 diastereomeric mixture of **2a** and **3a** as a colorless oil (0.239 g, 72%). The isomer ratio was determined by  $^1\text{H}$  NMR spectroscopy.

Further purification of diastereomers **2a-e** and **3a-f** was performed by preparative TLC with 4:1 hexane/ethyl ether or Kugelrohr distillation. The relative stereochemistry of diastereomers **2a-e** and **3a-f** was assigned by  $^1\text{H}$  NMR comparison with stereochemically defined authentic samples.

**syn- and anti-2-methoxy-1-phenyl-1-propanol (2a and 3a):** colorless oil<sup>16</sup> purified by Kugelrohr distillation at 105 °C (6 mmHg); IR (neat) 3400, 1080  $\text{cm}^{-1}$ ; MS  $m/z$  166 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) **2a**  $\delta$  0.98 (d, 3 H,  $J = 6.4$  Hz,  $\text{CH}_3$ ), 2.55 (br, 1 H, OH), 3.38 (dd, 1 H,  $J = 6.4$  and 7.8 Hz,  $\text{CHOMe}$ ), 3.43 (s, 3 H), 4.40 (d, 1 H,  $J = 7.8$  Hz,  $\text{CHOH}$ ), 7.25–7.36 (m, 5 H, Ph); **3a**  $\delta$  0.98 (d, 3 H,  $J = 6.4$  Hz,  $\text{CH}_3$ ), 2.15 (br, 1 H, OH), 3.42 (s, 3 H,  $\text{OCH}_3$ ), 3.54 (m, 1 H,  $J = 6.4$  and 3.4 Hz,  $\text{CHOMe}$ ), 4.91 (d, 1 H,  $J = 3.4$  Hz,  $\text{CHOH}$ ), 7.20–7.40 (m, 5 H, Ph).

**syn- and anti-2-methoxy-1,2-diphenylethanol (2b and 3b):** mp 84–87 °C (lit.<sup>17</sup> **2a** mp 53 °C; **3a** mp 100 °C); IR (KBr) 3400, 1030, 1045  $\text{cm}^{-1}$ ; MS  $m/z$  228 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) **2b**  $\delta$  2.45 (br, 1 H, OH), 3.30 (s, 3 H,  $\text{OCH}_3$ ), 4.12 (d, 1 H,  $J = 8.3$  Hz,  $\text{CHOMe}$ ), 4.65 (d, 1 H,  $J = 8.3$  Hz,  $\text{CHOH}$ ), 7.11–7.28 (m, 10 H, Ph); **3b**  $\delta$  2.45 (br, 1 H, OH), 3.22 (s, 3 H,  $\text{OCH}_3$ ), 4.34 (d, 1 H,  $J = 5.4$  Hz,  $\text{CHOMe}$ ), 4.88 (d, 1 H,  $J = 5.4$  Hz,  $\text{CHOH}$ ), 7.11–7.28 (m, 10 H, Ph).

**syn- and anti-1,2-diphenyl-2-isopropoxyethanol (2c and 3c):** mp 63–64 °C; IR (KBr) 3400, 1040  $\text{cm}^{-1}$ ; MS  $m/z$  256 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) **2c**  $\delta$  1.20 (dd, 3 H,  $J = 6.0$  and 8.0 Hz,  $\text{CH}_3$ ), 2.50 (br, 1 H, OH), 3.45–3.65 (m, 1 H,  $\text{CHMe}_2$ ), 4.30 (d, 1 H,  $J = 7.5$  Hz,  $\text{CHOPr}$ ), 4.65 (d, 1 H,  $J = 7.5$  Hz,  $\text{CHOH}$ ), 7.00–7.40 (m, 10 H, Ph); **3c**  $\delta$  1.03 (dd, 3 H,  $J = 3.0$  and 6.0 Hz,  $\text{CH}_3$ ), 2.48 (d, 1 H,  $J = 4.0$  Hz, OH), 3.35–3.65 (m, 1 H,  $\text{CHMe}_2$ ), 4.50 (d, 1 H,  $J = 5.5$  Hz,  $\text{CHOPr}$ ), 4.81 (dd, 1 H,  $J = 4.0$  and 5.5 Hz,  $\text{CHOH}$ ), 7.13–7.25 (m, 10 H, Ph). Anal. Calcd for  $\text{C}_{17}\text{H}_{20}\text{O}_2$ : C, 79.65; H, 7.86. Found: C, 79.52; H, 7.84.

**syn- and anti-1-methoxy-1-phenyl-2-propanol (2d and 3d):** colorless oil;<sup>18</sup> IR (neat) 3400, 1090  $\text{cm}^{-1}$ ; MS  $m/z$  166 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) **2d**  $\delta$  0.96 (d, 3 H,  $J = 5.9$  Hz,  $\text{CH}_3$ ), 1.66 (br, 1 H, OH), 3.24 (s, 3 H,  $\text{OCH}_3$ ), 3.79–3.85 (m, 2 H,  $\text{CHOMe}$  and  $\text{CHOH}$ ), 7.27–7.38 (m, 5 H, Ph); **3d**  $\delta$  1.10 (d, 3 H,  $J = 6.3$  Hz,  $\text{CH}_3$ ), 1.95 (br, 1 H, OH), 3.30 (s, 3 H,  $\text{OCH}_3$ ), 3.92–3.98 (m, 1 H,  $\text{CHOH}$ ), 4.11 (d, 1 H,  $J = 4.9$  Hz,  $\text{CHOMe}$ ), 7.27–7.38 (m, 5 H, Ph).

**cis- and trans-2-methoxycyclohexanol (2e and 3e):** colorless oil<sup>19</sup> purified by Kugelrohr distillation at 55 °C (4 mmHg); IR (neat) 3400, 1080  $\text{cm}^{-1}$ ; MS  $m/z$  130 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) **2e**  $\delta$  1.20–1.80 (m, 8 H,  $\text{CH}_2$ ), 2.26 (d, 1 H,  $J = 4.4$  Hz, OH), 3.25–3.30 (m, 1 H,  $\text{CHOMe}$ ), 3.37 (s, 3 H,  $\text{OCH}_3$ ), 3.82–3.88 (m, 1 H,  $\text{CHOH}$ ); **3e**  $\delta$  1.20–1.80 (m, 8 H,  $\text{CH}_2$ ), 2.78 (br, 1 H, OH), 2.90–2.98 (m, 1 H,  $\text{CHOMe}$ ), 3.40 (s, 3 H,  $\text{OCH}_3$ ), 3.38–3.45 (m, 1 H,  $\text{CHOH}$ ).

**meso-1,2-Diphenyl-1,2-ethanediol (3f).** To a solution of 0.24 g (1 mmol) of  $\text{Bu}_2\text{SnH}_2$  in THF (2 mL) was added 0.31 g (1 mmol) of  $\text{Bu}_2\text{SnCl}_2$  under  $\text{N}_2$ . The mixture was stirred at rt for 10 min. Ketone **1f** (0.57 g, 2 mmol) was added and this solution was stirred at 0 °C for 5 h. After quenching with MeOH (5 mL), the solvent was removed under reduced pressure. The residue was subjected to column chromatography with hexane-EtOAc (1:1) to give a desilylated alcohol **3f** (0.385 g, 90%): mp 135 °C (lit.<sup>20</sup> mp 135 °C); IR (KBr) 3350  $\text{cm}^{-1}$ ; MS  $m/z$  214 ( $\text{M}^+$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.18 (s, 2 H, 2 OH), 4.84 (s, 2 H, 2 CH), 7.15–7.35 (m, 10 H, Ph).

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**Supplementary Material Available:**  $^1\text{H}$  NMR spectra for compounds **2a-e** and **3a-f** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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### Hydrogenation and Dehydrogenation Reactions of Phenalenones and Dihydrophenalenones

Shikai Zhao, Jeremiah P. Freeman,\* and Jacob Szmuszkovicz\*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

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Interest in the phenalene system is due to its interesting chemical properties<sup>1</sup> and also to its potential as a template in drug design.<sup>2a,b</sup> During the course of our studies of phenalenes, 2,3-dihydro-1*H*-phenalene (**3**) was required as a starting material. Since catalytic hydrogenation has

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