Organotin Iodide Hydride: Chemoselective 1,4-Hydrostannations of Conjugated Enones in the Presence of Aldehydes and Subsequent Intermolecular Aldol Reactions

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The 1,2- and 1,4- regiochemistry of the reduction of conjugated enones has been intensively investigated with a variety of reductants.[1] Recently, efforts have been directed toward chemoselective reductions of conjugated enones with tolerance by susceptible functional groups. As exhibited in the reductions with $NaBH_4$, a general order of reactivity among carbonyl groups is conjugated enones < ketones < conjugated enals < aldehydes.[2,3] Not in keeping with this general reactivity order of aldehydes and conjugated enones, it is notable that the Luche reagent ($NaBH_4/LnCl_3$),[4] even in the presence of aldehydes, can reduce conjugated enones to furnish allylic alcohols in 1,2-fashion.[5] No selective 1,4-reduction of conjugated enones in the presence of aldehydes has been demonstrated, to our knowledge, although reductions by copper hydride tolerate the presence of ketone moieties in the same substrate.[6] If the 1,4-hydrometalation of conjugated enones could be accomplished in preference to the reduction of aldehydes, the subsequent aldol reaction of the resulting metal enolates could be expected. Organotin hydrides appear to be good candidates for this. They appear to act as soft Lewis acids leading to 1,4-addition,[7,8] and the resulting tin enolates can be expected to show pronounced reactivity toward aldehydes.[9] Quite recently, Enholm and co-workers have reported the selective 1,4-hydrostannation of cyclic enones by Bu_3SnH under free radical conditions and a subsequent intramolecular aldol reaction.[10] In this paper, we demonstrate that Bu_2SnIH reagents accomplish the selective 1,4-reduction of conjugated enones **1**, irrespective of coexistent aldehydes, and a subsequent diastereoselective intermolecular aldol reaction.

Tin iodide hydride reagents can be prepared by the two methods shown in eq 1, to obtain pure Bu_2SnIH (reagent A)[11] or an equimolar mixture of Bu_2SnIH and Bu_3SnI (reagent B).[12] The former (1 mmol) was synthesized by mixing Bu_2SnH_2 (0.5 mmol) and Bu_2SnI_2 (0.5 mmol) at room temperature in THF (1 mL). The latter (1 mmol) was prepared by mixing Bu_3SnH (1 mmol) and Bu_2SnI_2 (1 mmol) at room temperature in THF (1 mL). The complete formation of the Bu_2SnIH species was spectroscopically confirmed by ^1H, ^{13}C, and ^{119}Sn NMR.

$$Bu_2SnH_2 + Bu_2SnI_2 \longrightarrow \underset{\text{Reagent A}}{2\,Bu_2SnIH} \qquad \text{(eq.1)}$$

$$Bu_3SnH + Bu_2SnI_2 \longrightarrow Bu_2SnIH + \underset{\text{Reagent B}}{Bu_3SnI}$$

The selective 1,4-reduction of conjugated enone **1a** took place with either of these reagents (entries 1 and 2 in Table 1). Moreover, good enhancement of yield was achieved with reagent B, possibly because of the assistance of a soft Lewis acid, Bu_3SnI.[13] As shown in Table 1, these results are in sharp contrast with the original tin hydrides, Bu_2SnH_2 and Bu_3SnH. The former showed a lack of regioselectivity (entry 4), and the latter had poor reducing ability toward **1a** (entry 5). Other dibutyltin halide hydrides prepared in a manner similar to reagent B also effected the selective 1,4-reduction (entries 6 and 7), although the corresponding fluoride reagent predominantly promoted 1,2-reduction to furnish the allylic alcohol **3a** in 36% yield (entry 8). When 1,4-dinitrobenzene (DNB) was added as a radical scavenger, little effect on the 1,4-reduction of **1a** was observed (entry 3). This suggests that 1,4-hydrostannation by organotin iodide hydride proceeds by an ionic reaction path.

Table 2 lists the reductions of conjugated enones **1b**−**e** with reagent B in THF at ambient temperature. All runs demonstrated complete 1,4-selectivity to provide the

(1) The selective 1,2-reduction of conjugated enones has been carried out by aluminum hydrides such as $LiAlH_4$[a,b] and DIBAL-H,[c−f] and boron hydrides such as 9-BBN-H[g,h] and $NaBH_4$.[i,j] On the other hand, the selective 1,4-reductions have been accomplished by silicon hydrides,[k−n] copper hydrides,[o−r] iron hydrides,[s−v] and organoborohydrides such as L- and K-Selectride.[w,x] (a) Hudlicky, M. *Reductions in Organic Chemistry*; John Wiley & Sons, Inc.: New York, 1984; pp 119−121. (b) Balachander, N.; Wang, S. S.; Sukenik, N. *Tetrahedron Lett.* **1986**, *27*, 4849−4852. (c) Wilson, K. E.; Seidner, R. T.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1970**, 213−214. (d) Ashby, E. C.; Lin, J. J. *Tetrahedron Lett.* **1976**, 3865−3868. (e) Antus, S.; Gottsegen, A.; Nógradi, M. *Synthesis* **1981**, 574−576. (f) Zoretic, P.; Golen, J. A. *J. Org. Chem.* **1981**, *46*, 3555−3558. (g) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1975**, *40*, 1864−1865. (h) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 1197−1201. (i) Johnson, M. R.; Rickborn, B. *J. Org. Chem.* **1970**, *35*, 1041−1045. (j) Komiya, S.; Tsutsumi, O. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3423−3424. (k) Ojima, I.; Nihonyanagi, M.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Nakatsugawa, K. *J. Organomet. Chem.* **1975**, *94*, 449−461. (l) Keinan, E.; Greenspoon, N. *Tetrahedron Lett.* **1985**, *26*, 1353−1356. (m) Keinan, E.; Greenspoon, N. *J. Am. Chem. Soc.* **1986**, *108*, 7314−7325. (n) Schmidt, T. *Tetrahedron Lett.* **1994**, *35*, 3513−3516. (o) Boeckman, J. R. K.; Michalak, R. *J. Am. Chem. Soc.* **1974**, *96*, 1623−1625. (p) Semmelhack, M. F.; Stauffer, R. D. *J. Org. Chem.* **1975**, *40*, 3619−3621. (q) Semmelhack, M. F.; Stauffer, R. D.; Yamashita, A. *J. Org. Chem.* **1977**, *42*, 3180−3188. (r) Tsuda, T.; Fujii, T.; Kawasaki, K. Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1980**, 1013−1014. (s) Noyori, R.; Umeda, I.; Ishigami, T. *J. Org. Chem.* **1972**, *37*, 1542−1545. (t) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Brauman, J. I. *J. Am. Chem. Soc.* **1970**, *98*, 4685−4687. (u) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119−1140. (v) Boldrini, G. P.; Umani-Ronchi, A. *J. Organomet. Chem.* **1979**, *171*, 85−88. (w) Ganem, B. *J. Org. Chem.* **1975**, *40*, 146−147. (x) Fortunato, J. M.; Ganem, B. *J. Org. Chem.* **1976**, *41*, 2194−2200.

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(13) In the reaction with $Bu_3SnH/Pd(PPh_3)_4$, the yield increased using $ZnCl_2$ as the coactivating Lewis acid catalyst.[8b]

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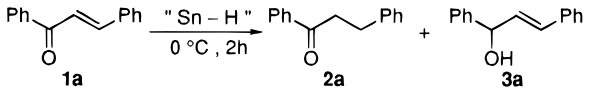
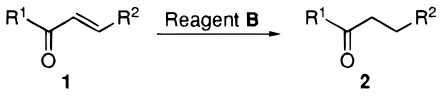
Table 1. Reductions of Chalcone 1a by Various Tin Hydrides



entry	"Sn−H"	yield, % 2a	3a
1	Reagent A[a]	69	0
2	Reagent B[b]	91	0
3	Reagent B− DNB[b,c]	77	0
4	Bu_2SnH_2	18	45
5	Bu_3SnH	19	0
6	$Bu_2SnBrH-Bu_3SnBr$[b]	53	0
7	$Bu_2SnClH-Bu_3SnCl$[b]	86	0
8	$Bu_2SnFH-Bu_3SnF$[b]	5	36

[a] Chalcone **1a** 1 mmol, Bu_2SnH_2 0.5 mmol, Bu_2SnI_2 0.5 mmol, THF 1 mL. [b] Chalcone **1a** 1 mmol, Bu_3SnH 1 mmol, Bu_2SnX_2 1 mmol, THF 1 mL. [c] DNB 0.1 mmol.

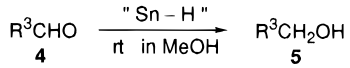
Table 2. Reductions of Various Conjugated Enones by Reagent B[a]



entry	R^1	R^2	1	conditions	yield %
1	Ph	Me	**1b**	rt, 2 h	**2b**, 72
2	Me	Ph	**1c**	rt, 2.5 h	**2c**, 67
3	Ph	H	**1d**	rt, 1 h	**2d**, 63
4	*cis*-cyclohexenone		**1e**	rt, 2 h	**2e**, 42 (4)[b]

[a] Enone **1** 1 mmol, Bu_3SnH 1 mmol, Bu_2SnI_2 1 mmol, THF 1 mL. [b] Cyclohexanol.

Table 3. Reductions of Aldehydes 4 by Various Tin Hydrides[a]



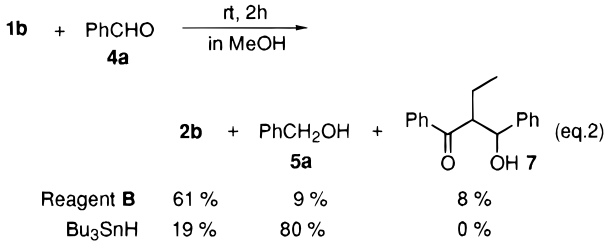
entry	aldehyde **4**		"Sn−H"	yield of **5**, %
1	R^3 = Ph	(**4a**)	Reagent A	**5a**, 5
2	R^3 = Ph	(**4a**)	Reagent B	**5a**, 6
3	R^3 = Ph	(**4a**)	Bu_3SnH	**5a**, 93
4	R^3 = Ph	(**4a**)	Bu_2SnH_2	**5a**, 100
5	R^3 = *c*-hex	(**4b**)	Reagent B	**5b**, 31
6	R^3 = *i*-Pr	(**4c**)	Reagent B	**5c**, 17

[a] Aldehyde **4** 1 mmol, SnH reagent 1 mmol, MeOH 1 mL.

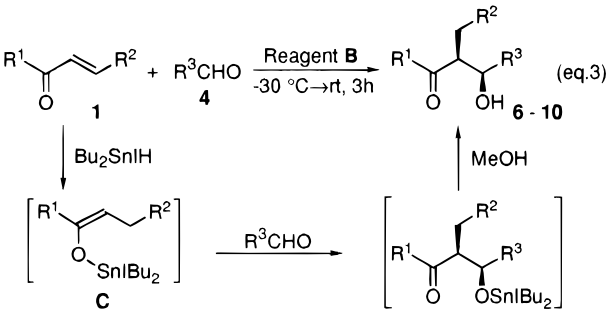
corresponding ketones **2b**−**e**; no allylic alcohols arising from 1,2-reduction were detected. In the case of cyclohexenone **1e** (entry 4), 4% of cyclohexanol was formed, plausibly generated by further reduction of the 1,4-reduction product.

Next we examined the reduction of aldehydes by these tin reagents. As shown in Table 3, the reagents A and B showed quite low reducing ability (entries 1 and 2), while either Bu_3SnH or Bu_2SnH_2 readily reduced benzaldehyde **4a** to benzyl alcohol **5a** (entries 3 and 4). Reagent B also exhibited poor reactivity toward cyclohexanecarboxaldehyde **4b** and isobutyraldehyde **4c** (entries 5 and 6).

This interesting outcome prompted us to try a competitive reduction of a conjugated enone and an aldehyde. When an equimolar mixture of **1b** (1 mmol) and benzaldehyde **4a** (1 mmol) was treated with reagent B in MeOH (1 mL) at ambient temperature, the selective 1,4-reduction of **1b** produced ketone **2b** in 61% yield without any 1,2-reduction, while benzyl alcohol **5a** was furnished in only 9% yield (eq 2). Surprisingly, the aldol product **7** was also obtained in spite of the MeOH solvent—the tin enolate had been expected to be quenched. In contrast, Bu_3SnH reduced aldehyde **4a** to **5a** in 80% yield (eq 2).

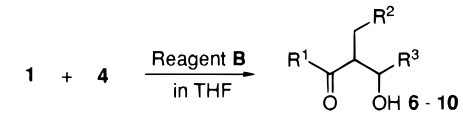


These results suggested that reagent B would be a good candidate for an intermolecular aldol reaction by the tin enolate (C), as illustrated in eq 3. As expected, when a mixture of **1a** and **4a** was treated with Bu_2SnI_2 and Bu_3SnH in THF at ambient temperature, aldol product **6** was obtained in 68% yield (entry 1 in Table 4). However, the



diastereoselectivity obtained at ambient temperature was not satisfactory (*syn*:*anti* = 38:62). The striking dependency of the diastereoselectivity on reaction temperature is indicated in entries 1 and 2 (Table 4). Excellent *syn*-selectivity was observed at −30 °C → rt (entry 2). This diastereoselectivity is not due to the Lewis acid, Bu_3SnI in reagent B, because the alternative use of reagent A also gave **8** with high *syn*-selectivity (entry 5).[14] It can be presumed that a (*Z*)-enolate is generated by the 1,4-hydrostannation of **1d** when in an *s-cis* conformation[15] and that the resulting (*Z*)-enolate gives the *syn* aldol

Table 4. Intermolecular Aldol Reactions of Conjugated Enones 1 with Aldehydes 4 by Using Reagent B[a]



entry	enone **1**	aldehyde **4**	conditions	yield, %	syn:anti[b]
1	**1a**	**4a**	rt, 2 h	**6**, 68	38:62
2	**1a**	**4a**	−30 °C → rt, 3 h	**6**, 47	80:20
3	**1b**	**4a**	−30 °C → rt, 3 h	**7**, 53	91:9
4	**1d**	**4a**	−30 °C → rt, 3 h	**8**, 74	89:11
5[c]	**1d**	**4a**	−30 °C → rt, 3 h	**8**, 55	90:10
6	**1d**	**4b**	−30 °C → rt, 3 h	**9**, 74	>99:1
7	**1d**	**4c**	−30 °C → rt, 3 h	**10**, 67	92:8

[a] Enone **1** 1 mmol, aldehyde **4** 1 mmol, Bu_3SnH 1 mmol, Bu_2SnI_2 1 mmol, THF 1 mL. [b] Determined by 400 MHz ^1H NMR. [c] **1d** 1 mmol, **4a** 1 mmol, Bu_2SnH_2 0.5 mmol, Bu_2SnI_2 0.5 mmol, THF 1 mL.

(14) It has been reported that the reaction of tributylstannyl enolate, analogous to the tin enolate C arising from 1,4-hydrostannation of **1c**, with **4a** gave moderate *anti*-selectivity at low temperature.[9]

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product under conditions of kinetic control.[16] The enones **1b** and **1d** also provided the aldol products **7** and **8**, respectively, with high *syn*-selectivities (entries 3 and 4). Moreover, cyclohexanecarboxaldehyde **4b** and isobutyraldehyde **4c** behaved similarly (entries 6 and 7).

In conclusion, Bu_2SnIH reagents selectively reduce conjugated enones **1** in the presence of aldehydes at ambient temperature. In addition, a subsequent aldol reaction proceeds with *syn*-selectivity at −30 °C. Further work on related systems including the characterization of the tin enolates C is underway.

Experimental Section

Analysis. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded at 400, 100, and 149 MHz, respectively. Samples for ^{1}H and ^{13}C NMR spectra of produced ketones and aldols were examined in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Samples for ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of tin hydrides were examined in tetrahydrofuran-d_8 containing tetramethyltin. GLC analyses were performed using FFAP and OV-1 (2-m x 3-mm) columns. Column chromatography was performed by using Wakogel C-200 mesh silica gel. Preparative TLC was carried out on Wakogel B-5F silica gel. Yields were determined by ^{1}H NMR or GLC using internal standards.

Materials. Tributyltin hydride (Bu_3SnH) and dibutyltin dihydride (Bu_2SnH_2) were, respectively, prepared by the reduction of tributyltin chloride (Bu_3SnCl) and dibutyltin dichloride (Bu_2SnCl_2) with $LiAlH_4$.[17] THF and toluene were freshly distilled over sodium benzophenone ketyl. All reactions were carried out under dry nitrogen.

Preparation of Organotin Iodide Hydrides. Reagent A (1 mmol) was synthesized by mixing Bu_2SnH_2 (0.5 mmol) and Bu_2SnI_2 (0.5 mmol) in THF. Reagent B (1 mmol) was prepared by mixing Bu_3SnH (1 mmol) and Bu_2SnI_2 (1 mmol) in THF. We spectrocopically confirmed that these reagents were immediately formed even at −50 °C.

Reagent A (8.00 M in THF-d_8): ^{1}H NMR (rt) δ 6.41 (Sn−H, $^1J(^{119}Sn-^1H)$ = 2060 Hz, $^1J(^{117}Sn-^1H)$ = 1968 Hz); ^{13}C NMR (rt) δ 14.1, 17.3 ($^1J(^{119}Sn-^{13}C_\alpha)$ = 408 Hz, $^1J(^{117}Sn-^{13}C_\alpha)$ = 390 Hz), 26.7 ($^3J(Sn-^{13}C_\gamma)$ = 74 Hz), 29.7 ($^2J(Sn-^{13}C_\beta)$ = 29 Hz); ^{119}Sn NMR (rt) δ −76.3 (d).

Reagent B (8.00 M in THF-d_8): ^{1}H NMR (rt) **Bu_2SnIH** δ 6.37 (Sn-H, $^1J(^{119}Sn-^1H)$ = 2046 Hz, $^1J(^{117}Sn-^1H)$ = 1955 Hz); ^{13}C NMR (rt) **Bu_2SnIH** δ 14.2, 17.2 ($^1J(^{119}Sn-^{13}C_\alpha)$ = 404 Hz, $^1J(^{117}Sn-^{13}C_\alpha)$ = 387 Hz), 26.8 ($^3J(^{119}Sn-^{13}C_\gamma)$ = 74 Hz, $^3J(^{117}Sn-^{13}C_\gamma)$ = 70 Hz), 29.8 ($^2J(Sn-^{13}C_\beta)$ = 29 Hz); **Bu_3SnI** δ 14.2, 17.4 ($^1J(^{119}Sn-^{13}C_\alpha)$ = 325 Hz, $^1J(^{117}Sn-^{13}C_\alpha)$ = 311 Hz), 27.2 ($^3J(^{119}Sn-^{13}C_\gamma)$ = 66 Hz,$^3J(^{117}Sn-^{13}C_\gamma)$ = 63 Hz), 29.8 ($^2J(Sn-^{13}C_\beta)$ = 24 Hz); ^{119}Sn NMR (rt) **Bu_2SnIH** δ −76.3 (d); **Bu_3SnI** δ 80.5 (s).

Representative Precedure for the 1,4-Selective Reduction of Enones. To the solution of Bu_2SnI_2 (1 mmol) in 1 mL of THF was added Bu_3SnH (1 mmol). The mixture was stirred at rt for 10 min. Conjugated enone **1a** (1 mmol) was added, and the solution was stirred until the Sn−H absorption disappeared in the IR spectra. After quenching the reaction with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column chromatography eluting with hexane−EtOAc (9:1) to give the product **2a**. Further purification was performed by TLC eluting with hexane−EtOAc (10:1).

1,3-Diphenylpropanone (2a): white solid; mp 68.7−70.3 °C; IR (KBr) 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.07 (t, 2H, J = 7.32 Hz), 3.30 (t, 2H, J = 7.32 Hz), 7.18−7.97 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 30.1, 40.4, 126.1, 128.0, 128.4, 128.5, 128.6, 133.0, 136.8, 141.3, 199.2; HRMS calcd for $C_{15}H_{14}O$ 210.1045, found 210.1024.

1,3-Diphenyl-2-propenol (3a): colorless liquid, purified by TLC eluting with hexane−EtOAc (4:1); IR (neat) 3200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.12 (br, 1H), 5.37 (dd, 1H, J = 6.35 and 2.44 Hz), 6.38 (dd, 1H, J = 16.11 and 6.35 Hz), 6.68 (d, 1H, J = 16.11 Hz), 7.20−7.44 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 75.1, 126.3, 126.6, 127.8, 127.8, 128.5, 128.6, 130.5, 131.5, 136.5, 142.8; HRMS calcd for $C_{15}H_{14}O$ 210.1045, found 210.1038.

Butyrophenone (**2b**) [495-40-9], 4-phenyl-2-butanone (**2c**) [2550-26-7], propiophenone (**2d**) [93-55-0], cyclohexanone (**2e**) [108-94-1], cyclohexanol [108-93-0] were identified in comparison with commercially available samples.[18]

Precedure for the Competitive Reaction between Enones and Aldehydes. To the solution of Bu_2SnI_2 (1 mmol) in 1 mL of MeOH were added **1b** (1 mmol) and **4a** (1 mmol). Bu_3SnH (1 mmol) was added, and the solution was stirred for 2 h. After quenching with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column chromatography, eluting with hexane−EtOAc (9:1) to give mainly ketone **2b** (61%); benzyl alcohol **5a** (9%) and aldol product **7** (8%) were also detected.

Representative Precedure for the Aldol-Type Reaction. To the solution of Bu_2SnI_2 (1 mmol) in 1 mL of THF were added conjugated enone **1** (1 mmol) and aldehyde **4** (1 mmol). Bu_3SnH (1 mmol) was added at −30 °C, and the solution was stirred for 3 h with warming to room temperature. After quenching with MeOH (5 mL), volatiles were removed under reduced pressure. The residue was subjected to column chromatography eluting with hexane-EtOAc (1:2) to give the corresponding products **6**−**10**. Further purification was performed by TLC eluting with hexane−EtOAc (1:1).

syn*- and *anti*-2-Benzyl-1,3-diphenyl-3-hydroxypropan-1-one (6):** colorless liquid, purified by TLC with hexane−EtOAc (1:1): IR (neat) 3400 and 1658 cm^{-1}; ^{1}H NMR ($CDCl_3$) ***syn δ 3.07 (dd, 1H, J = 3.90 and 13.67 Hz), 3.18 (dd, 1H, J = 10.74 and 13.67 Hz), 3.35 (d, 1H, J = 1.47 Hz), 4.00−4.07 (m, 1H), 5.08 (d, 1H, J = 4.39 Hz), 6.93−7.95 (m, 15H); ^{13}C NMR ($CDCl_3$) ***syn*** δ 33.5, 55.6, 74.0, 126.0, 126.2, 127.6, 128.1, 128.2, 128.2, 128.3, 128.9, 133.0, 137.3, 139.3, 141.6, 205.5; ^{1}H NMR ($CDCl_3$) ***anti*** δ 2.87 (dd, 1H, J = 6.35 and 13.68 Hz), 3.03 (dd, 1H, J = 8.79 and 13.68 Hz), 3.52 (d, 1H, J = 6.84 Hz), 4.07−4.12 (m, 1H), 4.95 (dd, 1H, J = 5.86 and 6.84 Hz), 6.94−7.94 (m, 15H); ^{13}C NMR ($CDCl_3$) ***anti*** δ 36.6, 54.7, 75.4, 126.1, 126.3, 127.7, 128.1, 128.3, 128.4, 128.4, 128.9, 133.0, 138.0, 138.5, 142.6, 204.7.

^{1}H and ^{13}C NMR data of *syn*-**6** were consistent with the ones reported previously: Boldrini, G. P.; Bortolotti, M.; Mancini, G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1991**, *56*, 5820−5826. Registry No. *syn*-**6**, 132455-70-0; *anti*-**6**, 135414-46-9.[18]

syn*- and *anti*-1,3-Diphenyl-2-ethyl-3-hydroxypropan-1-one (7):** colorless liquid, purified by TLC with hexane−EtOAc (1:1); IR (neat) 3250 and 1640 cm^{-1}; HRMS calcd for $C_{17}H_{18}O_2$ 254.1307, found 254.1304; ^{1}H NMR ($CDCl_3$) ***syn δ 0.77 (t, 3H, J = 7.57 Hz), 1.72−1.99 (m, 2H), 3.39 (br, 1H), 3.74 (m, 1H), 5.37 (d, 1H, J = 4.88 Hz), 7.16−7.86 (m, 10H); ^{13}C NMR ($CDCl_3$) ***syn*** δ 12.0, 20.6, 54.2, 73.8, 126.1, 127.3, 127.7, 128.1, 128.2, 128.5, 137.4, 142.1, 205.0; ^{1}H NMR ($CDCl_3$) ***anti*** δ 0.78 (t, 3H, J = 7.33 Hz), 1.46−1.75 (m, 2H), 3.29 (br, 1H), 3.76 (m, 1H), 4.99 (d, 1H, J = 7.33 Hz), 7.16−7.92 (m, 10H); ^{13}C NMR ($CDCl_3$) ***anti*** δ 11.5, 23.6, 54.3, 75.6, 126.3, 127.7, 128.2, 128.3, 128.5, 133.1, 138.2, 142.7, 205.6.

syn*- and *anti*-1,3-Diphenyl-3-hydroxy-2-methylpropan-1-one (8):** colorless liquid, purified by TLC with hexane−EtOAc (1:1); IR (neat) 3000 and 1705 cm^{-1}; HRMS calcd for $C_{16}H_{16}O_2$ 240.1151, found 240.1148; ^{1}H NMR ($CDCl_3$) ***syn δ 1.12 (d, 3H, J = 7.33 Hz), 3.63 (qd, 1H, J = 7.33 and 2.93 Hz), 5.17 (d, 1H, J = 2.93 Hz), 7.25−7.95 (m, 10H); ^{13}C NMR ($CDCl_3$) ***syn*** δ 11.1, 47.0, 73.1, 126.0, 127.3, 128.2, 128.5, 128.8, 133.6, 135.6, 141.8, 205.8; ^{1}H NMR ($CDCl_3$) ***anti*** δ 1.00 (d, 3H, J = 7.32 Hz), 3.88−4.07 (m, 1H), 4.93 (d, 1H, J = 7.81 Hz), 7.25−7.99 (m, 10H).

^{1}H NMR data of *syn*- and *anti*-**8** were consistent with the ones reported previously; Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598−1608. Registry No. *syn*-**8**, 71908-03-7; *anti*-**8**, 71908-02-6.[18]

syn*-3-Cyclohexyl-3-hydroxy-2-methyl-1-phenylpropan-1-one (9):** colorless liquid, purified by TLC with hexane−EtOAc (1:1); IR (neat) 3200 and 1630 cm^{-1}; HRMS calcd for $C_{16}H_{22}O_2$ 246.1621, found 246.1623; ^{1}H NMR ($CDCl_3$) ***syn δ 0.88−1.79 (m, 10H), 1.24 (d, 3H, J = 6.84 Hz), 2.06−2.15 (m, 1H), 3.10 (br,

(16) For example: Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1979**, *101*, 6120−6123.

(17) (a) Finholt, A. E.; Bond, A. C., Jr.; Wilzbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 2692−2696. (b) Kerk, G. J. M.; Noltes, J. G.; Luijiten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 366−369.

(18) Registry numbers are provide by the author.

1H), 3.64−3.71 (m, 2H), 7.26−7.97 (m, 5H); ^{13}C NMR ($CDCl_3$) ***syn*** δ 10.5, 25.8, 26.1, 26.3, 29.2, 29.4, 40.2, 41.3, 75.4, 128.4, 128.8, 133.4, 135.9, 205.9.

syn*- and *anti*-3-Isopropyl-3-hydroxy-2-methyl-1-phenylpropan-1-one (10):** colorless liquid, purified by TLC with hexane−EtOAc (1:1); IR (neat) 3350 and 1640 cm^{-1}; HRMS calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1301; ^{1}H NMR ($CDCl_3$) ***syn δ 0.96 (d, 3H, J = 6.35 Hz), 1.03 (d, 3H, J = 6.35 Hz), 1.25 (d, 3H, J = 6.83 Hz), 1.74−1.83 (m, 1H), 3.15 (d, 1H, J = 2.44 Hz), 3.62−3.71 (m, 2H), 7.45−7.98 (m, 5H); ^{13}C NMR ($CDCl_3$) ***syn*** δ 10.8, 18.9, 19.1, 30.7, 41.9, 76.6, 128.4, 128.7, 133.3, 135.9, 205.7; ^{1}H NMR ($CDCl_3$) ***anti*** δ 0.94 (d, 3H, J = 6.84 Hz), 1.00 (d, 3H, J = 6.84 Hz), 1.27 (d, 3H, J = 6.84 Hz), 1.74−1.85 (m, 1H), 1.89 (br, 1H), 2.97−3.00 (m, 1H), 3.56−3.62 (m, 1H), 7.45−7.98 (m, 5H); ^{13}C NMR ($CDCl_3$) ***anti*** δ 15.9, 16.9, 19.9, 31.2, 42.4, 79.1, 128.5, 128.7, 132.8, 136.7, 206.2.

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Supporting Information Available: Experimental procedures and ^{1}H and ^{13}C NMR and HRMS spectral data for the products **2a**, **3a**, **6**−**10** (21 pages). This material is contained in 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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